Published Monthly. Price, $5.00 per Annum.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

VOL. XVII.—NO. 5.
MAY, 1895.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE.
COMMITTEE ON PAPERS AND PUBLICATIONS.

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EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

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PAPERS ACCEPTED FOR PUBLICATION:

Methods of Indirect Analysis of Mixtures of Two Salts Having the Same Acid. By Edward K. Landis.

The Volumetric Determination of Zinc. By Geo. C. Stone.

The Proteids of the Rye Kernel. By Thomas B. Osborne.

The Proteids of Barley. By Thomas B. Osborne.

The Chemical Nature of Diastase. By Thomas B. Osborne.

On Some Conditions Affecting the Accuracy of the Determination of Potash as Potassium Platinochloride. By A. L. Winton.

Some Physical Aspects of the new Gas Argon the Ideal Thermometrical Substance. By W. R. Quinan.

H. B. Nason

After the cover of this issue had been printed the last number of the *Chemical News* containing Ramsay's announcement of the discovery of helium and argon in uraninite was received. The note on this subject, as well as that on the compounds of argon and the review of Clowe's Qualitative Analysis, do not, therefore, appear in the contents on the first page of the cover.

EDITOR.

H. B. Nason

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EDITOR.

Issued with May Number, 1895.

Proceedings.

BOARD OF DIRECTORS.

A charter for a Chicago Local Section was granted March 15.

NEW MEMBERS ELECTED MARCH 22.

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CHANGES OF ADDRESS.

Carlsson, Hugo, care of The Johnson Company, Lorain, Ohio.
Clark, Dr. John E., 18 John R. St., Detroit, Mich.
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Keller, Chas., 113 Biddle Ave., Station D., Pittsburg, Pa.
Simon, Dr. S. E., care of The Oscar A. Nenninger Company, Riverside Ave., near Second River, Newark, N. J.
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Wetmore, L. L., 35 Suffolk St., Holyoke, Mass.
Zinsser, Fred. G., 197 William St., New York City.

MEETINGS OF SECTIONS.

CINCINNATI SECTION.

March 15, 1895.

Vice-President Irwin J. Smith presided.

A communication was read from the Globe Soap Company announcing the death of W. G. Wallace. The Secretary was instructed to express the sympathy of the Section to the family of the deceased.

Professor T. H. Norton then proposed the following resolution:

Resolved, That this Section of the American Chemical Society deplores the loss which it has suffered through the death of one of its most earnest and active members, Mr. Lewis William Hoffmann, Chairman of the Committee on Analytical Chemistry, which occurred at Cincinnati on March 4, 1895.

Resolved, That the Section expresses to the family of the late Mr. Hoffmann its deep sympathy with them in their sudden bereavement.

Mr. John H. Westenhoff read a paper on the "Determination of Phosphorus in Ferro-Silicon." Mr. Westenhoff had experienced great difficulty in dissolving ferro-silicons in nitric or hydrochloric acid or aqua regia. He found by adding a small quantity of hydrofluoric acid to either nitric or hydrochloric acid, solution could be readily effected, and the determination could then be carried on by the usual method. Very satisfactory results were obtained and the time was shortened to that required for phosphorus determinations in pig iron.

Mr. Robert W. Hochstetter read a paper on "The Souring of Milk." He ascribed the souring of milk to the presence of bacteria and showed the chemical changes that took place. Results of analyses of a sample of milk, a portion of which was analyzed each day for five days, showed the amount of total solids decreased, the per cent. of fat was constant, while the acidity was variable and not proportional to the length of time milk had been standing. Electric discharges, produced over the surface of the milk for several hours, seemed to have little or no effect, and Mr. Hochstetter thought the souring of milk during thunder storms was due to the fact that the atmospheric condi-

tions were more favorable to the growth of the bacilli. He found that milk cooled quickly, as soon as drawn from the mammary gland, was not liable to sour during thunder storms.

Mr. E. Twitchell was elected Chairman of the Committee on Analytical Chemistry to fill the vacancy caused by the death of Lewis W. Hoffmann.

WASHINGTON SECTION.

Thursday, February 14, 1895.

President Charles E. Munroe in the chair.

The meeting was devoted mainly to the address of the retiring President, Dr. Wm. H. Seaman. His subject was "Chemistry in Education," which was considered under four heads: (1) What is chemistry, (2) what are its relations to common life, (3) how much chemistry is actually taught in our schools, and (4) what should be taught there. After the delivery of the address, it was resolved to co-operate with the other scientific societies in enlarging the powers of the joint commission, and the adoption of a constitution for the joint commission based upon its being composed of the officers and administrative boards of the several component societies.

Thursday, March 14, 1895.

President Charles E. Munroe in the chair; thirty-five members present; Mr. G. E. Barton was elected to membership.

Professor F. W. Clarke gave a brief account of his general theory concerning the constitution of the silicates. His work will appear in full as a bulletin of the U. S. Geological Survey. Parts of it have already appeared in this JOURNAL.

Dr. H. N. Stokes read a paper on the "Chloronitrides of Phosphorus and the Metaphosphimic Acids." The paper was a contribution to the subject of homology and polymerism of inorganic compounds. It was shown that Liebig's chloronitride of phosphorus, $P_3N_3Cl_6$ is but one member of an homologous series of chloronitrides, having the general formula $(PNCl_2)_x$, two others of which were described; *viz.*, $(PNCl_2)_4$ and another of

unknown molecular weight. The chloronitrides $(PNCl_2)_3$ and $(PNCl_2)_4$, by saponification, yield trimetaphosphimic acid, $(PNO_2H_2)_3$, and tetrametaphosphimic acid, $(PNO_2H_2)_4$, which may be regarded as members of an homologous series of acids parallel with the metaphosphoric acid series, and having one-third of the oxygen of the latter replaced by the amide group. These acids being derived from chlorides containing the nuclei $(PN)_x$ may be regarded as polymers of the simplest form PNO_2H_2, in which nitrogen atoms serve as connecting links between the phosphorus atoms.

Dr. J. E. Blomén read a paper "On the Manufacture of Soluble Nitrocellulose for Nitrogelatine and Plastic Dynamite."

VOL. XVII. MAY, 1895. NO. 5.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

HENRY BRADFORD NASON.

Henry Bradford Nason, Professor of Chemistry and Natural Science at the Rensselaer Polytechnic Institute, Troy, N. Y., died of apoplexy, at his home, on January 17, 1895.

Professor Nason was a former president of the American Chemical Society, and for very many years an active, interested, and energetic member.

During the early days of the Society, long before it had acquired its present established footing, he stood as one of its staunch supporters, and never despaired of its eventual and permanent success; a faith which to-day has become reality.

Those who were so fortunate as to know Professor Nason personally, will remember with pleasure that scientific attainments were associated in him with a cheerful and kindly nature, eminently qualified to win many and lasting friends.

He was the son of Elias and Susanna (Keith) Nason, and was born at Foxborough, Norfolk County, Mass., June 22, 1831. In November, 1841, he moved to North Bridgewater, Mass., the native place of his mother, who died the year previous. In 1843 he attended a school for boys kept by Mr. Savory at Newburyport, Mass. From 1844 to 1847 he attended the Adelphian Academy at North Bridgewater, now Brockton, Mass. In December, 1847, he entered Williston Seminary, Easthampton, Mass., graduating in 1851. He entered Amherst College and graduated in 1855. September 1, 1855, he sailed from New York to London on the ship Amazon, having a passage of thirty-five days. He travelled through Holland, Belgium, up the Rhine to Frankfort

and then to Göttingen, where he was matriculated as a student of philosophy October 24, 1855. While connected with the university he devoted his time to chemistry, mineralogy, and geology, and attended lectures on physics and botany, graduating in the Summer of 1857. He spent a short time at Heidelberg and Freiburg and then visited Berlin, Paris, and London. He spent the Winter of 1857–58 in teaching at the Raymond Collegiate Institute, Carmel, Putnam County, N. Y. In April, 1858, he was appointed professor of natural history in the Rensselaer Polytechnic Institute. In the Summer he declined an appointment as professor of chemistry and natural science in Oahu College, Hawaiian Islands. He accepted an appointment to the same chair in Beloit College, Wisconsin, in September, 1858, and spent a part of each year there, the remainder of the time at Troy, until 1866, when he resigned the position at Beloit to accept the professorship of chemistry and natural science at the institute, which position he held until his death.

From 1855 to 1857, while connected with the university at Göttingen, during vacations he made the tour of Europe. In the Spring of 1860 he travelled through the southern portion of the United States. He sailed for Europe in July, 1861, and travelled through Great Britain, and afterward went to Italy, Sicily, and southern France, spending considerable time in the study of volcanic phenomena. He spent the Summer of 1872 in California, Nevada, and Idaho. In the Autumn he made a second visit to California, visiting the mining regions of Colorado and Utah. In 1875 he made a third trip to California, visiting the Yosemite, northern California and Nevada. He spent the Summer of 1877 in visiting northern Europe, Finland, and Russia.

In 1877 Professor Nason was appointed by President Hayes juror for the United States Government at the Paris Exposition and was assigned the department of mineralogy and metallurgy.

In 1884 he visited northern Europe and the fiords and glaciers of Norway, extending his travels to the North Cape.

Professor Nason published "Inaugural Dissertation on the Formation of Ether," 1857; "Table of Reactions for Qualitative Analysis," 1865; translated and revised "Wohler's Handbook

of Mineral Analysis," 1868; "Table for Qualitative Analysis in Colors," 1870; edited Elderhorst's "Manual of Blowpipe Analysis," 1873; fourth and fifth editions of the same, 1875–76; edited "Manual of Blowpipe Analysis and Determinative Mineralogy," 1880; compiled "Semi-Centennial Catalogue of the Rensselaer Polytechnic Institute," 1874, and edited "Proceedings of the Semi-Annual Celebration" of the same institution, 1874; edited "Biographical Record of the Officers and Graduates of the Rensselaer Polytechnic Institute," 1886.

In 1857 he received the degree of A.M. and Ph.D. from the Georgia Augusta University, Göttingen; in 1864 the honorary degree of A.M. from Amherst College; in 1880 the honorary degree of M.D. from the Union University of New York, and the same year the honorary degree of LL.D. from Beloit College, Wisconsin. He has been elected fellow of the American Association for the Advancement of Science, fellow of the London Chemical Society, fellow of the Society of Chemical Industry, England, member of the American Chemical Society, corresponding member of the New York Academy of Science, member of the American Institute of Mining Engineers, member of the Troy Scientific Association, honorary member of the Albany Institute, member of the Norske Turistforenings, Christiana, Norway; elected member of the University Club, 1883, and of the Union League Club, New York City, 1886.

W. P. MASON.

METHODS FOR THE DETERMINATION OF MANGANESE.[1]

By W. S. Thomas.

Received February 11, 1895.

FOR some time no satisfactory method for the rapid determination of manganese has been in use in this laboratory; all proposed schemes have been, from time to time, successively tried and none have withstood the tests under all conditions.

With the great demand now made for chemical analyses by which metallurgical and manufacturing processes are controlled, it has been no small part of the chemist's work to devise rapid methods for making these determinations, so necessary for the information of the metallurgist and manufacturer.

[1] This and the paper following it are reprinted from the Bulletin of the Missouri Mining Club, published at the Missouri School of Mines, Rolla, Mo.

In order to supply this need, every rapid method now in use and generally known or published, has been introduced into the course of instruction known as Technical Analysis in this laboratory.

During the past two years the determination of manganese has been attempted by using a method published in the *Journal of Analytical and Applied Chemistry* by A. H. Low, but so far as the method has been applied in this laboratory it has proven of no value, owing to the low results obtained.

For the purpose of arriving at a satisfactory conclusion in regard to the Low method, a series of experiments were begun, using manganese carbonate, and manganese sulphate, from which most of the water of crystallization was driven off and the sample kept in a corked tube. In order to check the volumetric work the metallic content of both salts was carefully determined by gravimetric analyses, in which the manganese was precipitated as manganese ammonium phosphate, ignited, and weighed as pyrophosphate.

This method gave very closely agreeing results by duplicate analyses of the respective salts, the filtrate in each case being tested for manganese by means of ammonium sulphide and only mere traces of manganese found.

A standard solution of potassium permanganate was made in which 6.312 grams of potassium permanganate were dissolved in two liters of distilled water, and a solution of 11.46 grams of $C_2H_2O_4 + 2H_2O$, (oxalic acid), in one liter of distilled water, kept well corked and away from the light.

In obtaining an experimental standard, ten cc. of the oxalic acid solution were taken and five cc. of sulphuric acid added, and the whole titrated with standard potassium permanganate, one cc. = 0.0056 gram of iron, the strength of the oxalic acid being calculated from the data obtained.

It was found that ten cc. of oxalic acid reduced 20.1 cc. of the standard potassium permanganate, one cc. of which equals 0.0011 gram manganese, based on the equation $10FeSO_4 = K_2Mn_2O_8$. Therefore one cc. oxalic acid equals 0.002211 gram manganese.

By calculation based upon the equation (Low's)

$$C_2H_2O_4, 2H_2O + MnO_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O,$$

126 parts of oxalic acid equal fifty-five parts of manganese. Knowing the weight of oxalic acid in one cc. of solution and introducing this into the proportion, one cc. of oxalic acid solution was found to be equivalent to 0.005 gram manganese.

From these two methods we obtain two entirely different strengths, neither of which give satisfactory results, as will be seen by calculations based upon titrations, made according to Low's instructions.

A half gram of manganese sulphate, which gave 34.64 per cent. manganese by gravimetric analysis, was taken and made up to 500 cc.; fifty cc. were taken for each titration, zinc oxide was added in the usual way, and bromine water to precipitate the manganese as manganese dioxide, the excess of bromine boiled off, solution filtered, the precipitate well washed with hot water, and the filter with its contents replaced in the flask where the precipitation was made; fifty cc. of dilute sulphuric acid added and a measured volume of oxalic acid run in from a burette; the excess of oxalic acid determined by treating with the standard potassium permanganate. Nine titrations by Low's method gave the following results:

No.	$C_2H_2O_4 2H_2O$ added.	Excess of $K_2Mn_2O_8$.
1	10 cc.	13.6 cc.
2	10 "	13.6 "
3	10 "	13.4 "
4	10 "	13.6 "
5	10 "	13.8 "
6	10 "	13.5 "
7	10 "	13.8 "
8	10 "	13.8 "
9	10 "	14.0 "

Taking a mean of the excess as 13.6 cc. of potassium permanganate, and multiplying by 0.0011 (one factor of the strength of the permanganate) and dividing by 0.002219 the strength of one cc. of oxalic acid in terms of potassium permanganate, we obtain the amount of oxalic acid oxidized by the 13.6 cc. of potassium permanganate, which, subtracted from ten cc. gives the number of cubic centimeters of oxalic acid oxidized by the manganese dioxide derived from the sample. Multiplying this by 0.0055+ and correcting for one gram, we obtain 35.64, which is

one per cent. above the gravimetric result as the per cent. of manganese in the sample. The factor $2\frac{1}{2}$ used in this calculation is obtained by comparing the two equations:

$$2C_2H_2O_4,2H_2O + 2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 4CO_2 + 8H_2O$$

$$5C_2H_2O_4,2H_2O + K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O,$$

from which is readily seen, that the strength of one cc. of oxalic acid in terms of potassium permanganate is $2\frac{1}{2}$ of its strength in terms of manganese dioxide, from which we can derive a strength for oxalic acid based on experiment and not on calculation, as set forth in another place.

Titrating the same sample of manganese sulphate by Volhard's method, in which the strength of the potassium permanganate in terms of iron equal to 0.0056 gram, is multiplied by the factor 0.2946, which is obtained by comparison of the equations:

$$10FeSO_4 + 8H_2SO_4 + K_2Mn_2O_8 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3$$

$$3MnO + K_2Mn_2O_8 = 5MnO_2 + K_2O$$

(in which $K_2Mn_2O_8 = 10FeO$ and $3MnO$ respectively) the following results were obtained: One-half gram of substance taken and made up to 500 cc. and fifty cc. taken for each titration.

No. of titration.	Cubic centimeters of $K_2Mn_2O_8$ used.
1 50 cc. solution.	10.3
2 50 cc. solution.	10.3
3 50 cc. solution.	10.3

Multiplying this result by 0.2946 and correcting for one gram we get thirty-four per cent. manganese or 0.64 per cent. less than by the gravimetric analyses.

The methods were both tried upon a sample of manganese carbonate, which gave, by means of manganese pyrophosphate, forty-five per cent. of manganese. Several samples of one-half gram were taken and a few titrations made from each with the following results. Six titrations by Low's method gave

No.	$C_2H_2O_4 2H_2O$ added.	Excess of $K_2Mn_2O_8$.
1	10 cc.	12.9 cc.
2	10 "	12.6 "
3	10 "	13.0 "
4	10 "	12.3 "
5	10 "	12.3 "
6	10 "	12.9 "

Throwing out No. 3, the average volume of potassium permanganate reduced by the excess of oxalic acid equals 12.6 cc. and applying the same calculations as before, we obtain 41.03 per cent., or four per cent. less than by gravimetric analyses.

Eight titrations by Volhard's method gave the following results:

No.	Solution.	$K_2Mn_8O_8$ added.
1	50 cc.	13.5 cc.
2	50 "	13.5 "
3	50 "	13.5 "
4	50 "	13.4 "
5	50 "	13.5 "
6	50 "	13.4 "
7	50 "	13.5 "
8	50 "	13.5 "

When corrected for one gram these titrations give 44.54 per cent. manganese, or 0.46 per cent. less than the gravimetric analyses.

The results obtained with Low's method are in one case approximate, but, when the same manipulations are applied to as much as one-half gram of substance, the result is nearly fifty per cent. too low. Theoretically the method is perfect, but I have been unable to obtain the theoretical results in practice, and in so far as this is the important feature, the method has proved worthless in my work.

Volhard's process is very rapid and simple in its application. The manganese should be in the form of a proto salt, which is the form obtained by the procedure in decomposing an ore. Iron is removed by means of zinc emulsion, $3ZnO + Fe_2Cl_6 = Fe_2O_3 + 3ZnCl_2$, which converts the iron into insoluble ferric oxide by vigorous shaking.

This having been done, the solution, precipitate and all, is made up to 500 cc.; fifty cc. is taken out by means of a pipette, placed in a twelve-ounce flask, 250 to 300 cc. of hot water added, heated to boiling, standard potassium permanganate run in, and the solution shaken after each addition of potassium permanganate. A bulky brown precipitate of manganese dioxide is formed and the pink color of the solution is destroyed until the manganese is all oxidized to manganese dioxide, when a drop of

the permanganate imparts a pink color to the solution. A few trials will enable the operator to ascertain this point with accuracy and rapidity.

This work was conducted more for the purpose of ascertaining the values of the methods when working with the rapidity which is required in actual practice, than for absolute accuracy, to 0.01 or 0.001 per cent. I have no doubt that Volhard's process can be made to check closer than 0.64 or 0.46 per cent. respectively, of the metallic content of an ore, but in practical metallurgical analyses, it is not always practicable to exercise the necessary precautions. The method is capable of wide application, and where rapidity is essential, is sufficiently accurate in most, if not all cases.

THE WET ASSAY FOR COPPER.

By R. S. Dulin.

Received February 11, 1895.

IT seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognized methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say, that either method in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are :

1. The cyanide method. 2. The iodide. 3. The electrolytic. A colorimetric method is also employed for the determination of copper, when the percentages fall below two per cent. I have made no particular study of this method, and as it is only employed in special cases, I shall make no further reference to it.

The cyanide method depends upon the fact, that when a solution of potassium cyanide is run into an ammoniacal solution of copper the blue color is discharged. The reaction is as follows:

$$(NH_4)_2(NH_3)_2CuO(NO_3)_2 + 4KCN + 3H_2O = K_2Cu(CN)_4 + 2KNO_3 + 4NH_4OH.$$

This method is fully described in Furman's Manual of Practical Assaying. The following precautions should always be carefully observed. 1. The bulk of the liquid titrated should always be uniform. By inattention to this an error of from two to three per cent. is possible. 2. The solution should always be cooled to the temperature of the laboratory before titrating, otherwise an error of about three per cent. is possible. 3. The amount of ammonia added should be nearly constant, otherwise the possible error may amount to as much as five per cent., or even more.

These precautions are general and must always be carefully observed, in every modification which may be made in the method. In the ordinary modification of the method, ferric hydroxide is almost certain to be precipitated, upon the addition of the ammonium hydroxide. If the amount be small, no error is apt to occur, but it should always be filtered off. If the amount be large, it is not easy to wash out all of the copper salt, thereby causing lower results, unless large quantities of wash-water are employed, thus increasing and varying the bulk. The error arising from increased bulk may be obviated, by taking, after mixing, an aliquot part of the solution; if the solution be not thereby made very dilute, the error is so slight that it may be neglected. If salts of manganese are present, the end reaction cannot be determined, owing to the liquid first turning green, finally black. The presence of large quantities of calcium, I found, confused the end reaction, causing error of importance. Experiments made showed that magnesia did not interfere, and the presence of antimony and arsenic was found to cause no sensible variations.

Zinc, which is almost certain to be present in varying amount, is a possible source of great error. The following results were obtained from a large number of carefully conducted experiments. Only the averages are given and they are substantially the same as the extremes. In these experiments the bulk of the liquid varied from twenty-five to as much as fifty cc., thereby causing a slight error, for which no correction has been made. This error would not substantially change the results. Careful attention was paid to the precautions previously enumerated.

Weight of copper.	Weight of zinc.	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	11.0 "	0.6 cc.
0.05	0.02	11.7 "	1.3 "
0.05	0.03	12.3 "	1.9 "
0.05	0.04	12.9 "	2.5 "
0.05	0.05	14.0 "	3.6 "
0.05	0.06	16.1 "	5.7 "
0.05	0.07	18.9 "	8.5 "
0.05	0.08	21.6 "	11.2 "
0.05	0.09	24.3 "	13.9 "

These results show that there is a gradual increase of about six-tenths cc. in the amount of the cyanide solution required, until the amount of zinc present nearly equals the amount of copper, when the increase becomes variable, until the amount of zinc becomes greater than the amount of copper to the extent of twenty per cent., when the increase, though larger, about two and seven-tenths cc., again becomes regular.

The effects of cadmium are similar, as shown by the following results, which are also the averages of a large number of experiments, in which the extremes are farther removed from the mean than was found with zinc. As in the preceding experiments the precautions previously enumerated were very carefully observed, except in the case of bulk, in which the variations were identically the same as with the experiments with zinc.

Weight of copper.	Weight of cadmium.	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	10.6 "	0.2 cc.
0.05	0.02	10.8 "	0.4 "
0.05	0.03	11.1 "	0.7 "
0.05	0.04	11.6 "	1.2 "
0.05	0.05	12.0 "	1.6 "
0.05	0.06	12.4 "	2.0 "
0.05	0.07	13.5 "	3.1 "
0.05	0.08	14.5 "	4.1 "

These results show that there is a gradually accumulating increase in the consumption of cyanide due to the presence of cadmium. As cadmium is a constituent usually found associated with copper, it must be removed, if reliable results be required. Silver also interferes, but in a regular way. If the amount of silver be known, by previous assay, it is best allowed for by calculation.

The following modification of the cyanide method has been thoroughly tested, under the immediate supervision of Prof. Seamon, and it is recommended as giving results equal in value to those obtained by the electrolytic method.

The ore is treated according to the method described on page 161 of Furman's Manual of Assaying. In this way a solution of the copper salt is obtained, practically free from lead and silver. This solution is boiled with strips of aluminum foil, resulting in the complete precipitation of the copper together with any silver which may remain in the solution, which is always so small as to be negligible, as I have demonstrated by a number of experiments upon different ores. If cadmium be present, it is only partially precipitated, beginning after the copper is thrown down. If care be taken to stop the boiling, immediately after the copper is precipitated, which can be determined with constant practice, by the eye, the amount of cadmium precipitated is so small as not to cause sensible error. The liquid is decanted from off the aluminum foil and copper, quickly washed several times with hot water, care being taken not to wash away any particles of the copper; three cc. of nitric acid are then added to the flask and boiled to dissolve the copper, the solution is then treated with ammonium hydroxide as in the usual way and titration is made with the usual solution of cyanide.

This method has been very carefully tested and the results were so satisfactory, and nearly uniform, that I recommend it as being as accurate as the electrolytic method, under the conditions in which the latter is usually employed.

The iodide method is most commonly employed in the Lake Superior district and in foreign countries, where it is regarded with much favor. Many chemists regard it as more accurate than the cyanide or electrolytic methods, and there is no doubt

from my experiments that it is more accurate than the ordinary modification of the cyanide and equal to that of the electrolytic. The method depends upon the following reactions:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2I + 2K_2SO_4$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

The best results are obtained when the copper is precipitated with aluminum foil, as previously described under the cyanide method. The method is fully described in Furman's Manual of Assaying, and I only desire to call attention to the necessity for attending to the following precautions:

1. The presence of iron in about equal amounts with the copper requires more "hypo," increasing the amount of copper to the extent of two to three per cent. 2. The solution should be titrated cold. 3. The presence of large amounts of alkaline salts, particularly sodium sulphate, decreases the amount of copper. 4. The presence of bismuth clouds the end reactions. My experience with the modification of this method, in which the copper is first precipitated with aluminum foil convinces me that with this change the results are as accurate as those obtained with the modified cyanide method; but it is not so rapid, owing to the time lost at various stages; this is an important factor in the adoption of any method for metallurgical work, when thirty and forty assays must be completed every day. The method is a little more difficult to manipulate than the cyanide method

The electrolytic method is perhaps the most highly favored in this country. It has the reputation for greatest accuracy. It requires more time than either of the other, but since it is easy to regulate the work, so that the battery will precipitate during the night, this is not of so much importance. In regular routine work after solution is effected, the copper should be precipitated with hydrogen sulphide, otherwise many interfering metals are apt to be present and deposited with the copper. I have found that errors from this source are largely, if not entirely, eliminated, if deposition be made from a solution containing a large amount of nitric acid. My best results were obtained when I added twenty cc. of strong nitric to about 150 cc. of solution. This holds up the other metals, but a stronger cur-

rent is required to precipitate all of the copper and more attention must be paid to proper and rapid manipulation after precipitation. This method is much improved by previously precipitating the copper from its solution by boiling with aluminum foil and then redissolving the copper in nitric acid. The following results, obtained from the same sample, carefully prepared, obtained by the three methods, furnish a fair idea of the relative values of the several methods.

A copper matte, containing 20.15 per cent. of copper, as determined by a large number of analyses, made by several different assayers, and by different methods, was run by each method. The amount of copper in the second matte, determined from the same data, was found to be twenty-eight per cent., while the per cent. of copper in the ore was 30.18 per cent.

The results obtained by the cyanide method were respectively 20.15 per cent., 27.95 per cent., and 30.20 per cent. The copper was first precipitated with the aluminum foil. The same substances, with the iodide method, first precipitating with aluminum foil, gave, respectively, 20.25, 28.35, and 30.3 per cent. By the electrolytic method, the same substances gave, respectively, 20.045, 28.15, and 30.05 per cent.

These results justify the statement that the iodide method with the aluminum modification gives results usually one-tenth to three-tenths per cent. too high, while the electrolytic method is too high or too low, according to the amount of metallic substances present precipitable by the electric current; and the cyanide method gives results which are practically correct.

ON THE STANDARDIZATION OF SULPHURIC ACID.

By F. S. Shiver.

Received February 16, 1895.

M. WEINIG[1] has described a method for the standardization of sulphuric acid by means of weighing the $(NH_4)_2SO_4$ obtained by mixing an accurately measured quantity of the sulphuric acid solution with an excess of ammonia, evaporating, drying, and weighing. His method of procedure is as follows: To an accurately measured quantity of the sulphuric acid solution, ammonia in slight excess is added, the solution evaporated to dryness, dried for half an hour at 115°–

[1] Ztschr. angew. Chem., *1892*, 204, 205; *J. Chem. Soc.*, 64, 2, 145.

120° C., cooled in a desiccator, and weighed as ammonium sulphate ($(NH_4)_2SO_4$). Recognizing the tendency of ammonium salts to decompose, especially when in aqueous solution and in the presence of heat, I was rather uncertain whether, by the mode of procedure just described, one would obtain the normal sulphate. Watts says concerning ammonium salts: "Their aqueous solution, when exposed to the air (still more rapidly when evaporated) generally loses ammonia, an acid salt or a normal salt mixed with excess of acid, being formed; hence, in crystallizing an ammonium salt, ammonia must be added occasionally during the evaporation." I therefore decided to make some experiments in this connection since it was of primary importance that the salt weighed should be the normal sulphate ($(NH_4)_2SO_4$). Four portions of twenty cc. each of the $\frac{N}{4}$ sulphuric acid solution were accurately measured out and treated as directed by Weinig.

Results were as follows:

I.	0.3987	gram	sulphur	trioxide	in	twenty	cc.	of	$\frac{N}{4}$	sulphuric	acid.
II.	0.3989	"	"	"	"	"	"	"	"	"	"
III.	0.3990	"	"	"	"	"	"	"	"	"	"
IV.	0.3992	"	"	"	"	"	"	"	"	"	"
Aver.	0.3990	"	"	"	"	"	"	"	"	"	"

These residues tested with delicate litmus seemed to be feebly acid; to further test this point, four portions of twenty cc. each of this same acid were measured out and treated as follows: The acid solution was made alkaline with ammonia in excess and evaporated down to dryness; the dish was then removed from the bath and its contents thoroughly moistened with strong ammonia water, preferably 0.96 sp. gr.; this will avoid the spattering occasioned by the use of concentrated ammonia water and is just as effective as the latter; the dish was then replaced on the bath and allowed to remain until its contents appeared quite dry, then removed and dried for half an hour at 110°–120° C., cooled in a desiccator, and weighed; the drying repeated for another half hour at the same temperature, cooled, and weighed; no further loss of weight occurred from this second drying in these experiments but I think it safer to weigh the second time, else one is left in doubt as to the thorough desiccation of the ammonium sulphate. The results by this method of treatment are as follows:

I.	0.3996	gram	sulphur	trioxide	in	twenty	cc.	$\frac{N}{4}$	sulphuric acid.
II.	0.4001	"	"	"	"	"	"	"	"
III.	0.3993	"	"	"	"	"	"	"	"
IV.	0.3992	"	"	"	"	"	"	"	"
Average	0.3996	"	"	"	"	"	"	"	"

These residues tested with delicate litmus were neutral. It will be seen then that the results by the second mode of treatment are slightly higher in nearly all cases than those obtained by the first method described. In further proof of the slight decomposition that takes place when an aqueous solution of ammonium sulphate is evaporated to dryness, I took one of the residues obtained by the second method just described and added about as much water as there was present in the first evaporation; this solution was evaporated to dryness, dried as already described, cooled, and weighed; the weight of ammonium sulphate before adding water and second evaporation was 0.6591 gram, after adding water and second evaporation 0.6581 gram, a loss of 0.0010 gram ammonium sulphate; the amount of sulphur trioxide calculated from this weight of ammonium sulphate, *viz.*, 0.6581 gram, will be seen to agree quite closely with the results secured by the first method described, in which there seems to be some slight decomposition of the ammonium sulphate.

Therefore from these experiments there seems to be some slight decomposition produced when an aqueous solution of ammonium sulphate is evaporated to dryness and in order to be sure to obtain the normal salt, it is necessary, in my experience, to moisten thoroughly with ammonia water the residue as has been described and then to dry and weigh in the manner directed. The decomposition noticed and the error in results occasioned by it is slight, though the results in most cases are lower than those obtained when precaution is taken to prevent this decomposition by moistening with ammonia water as has been described.

The results of this method compared with the precipitation by barium chloride and weighing as barium sulphate are quite close and satisfactory. In one cc. of $\frac{N}{4}$ sulphuric acid there was found by the barium chloride method 0.02007 gram sulphur trioxide equivalent to 0.00855 gram ammonia. The ammonium sulphate

method, as carried out by myself, gives 0.01998 gram sulphur trioxide equivalent to 0.00851 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.35 cc. of which equals twenty cc. of the $\frac{N}{4}$ sulphuric acid) is equivalent to 0.003396 gram ammonia by the barium chloride method and by the ammonium sulphate method as carried out by myself 0.003380 gram ammonia.

Another solution of $\frac{N}{4}$ sulphuric acid was tested by the two methods.

In one cc. of the solution there was found by the barium chloride method 0.01977 gram sulphur trioxide equivalent to 0.008421 gram ammonia.

The ammonium sulphate method, as carried out by myself, gives 0.019895 gram sulphur trioxide equivalent to 0.008474 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.25 cc. of which equals twenty cc. of the $\frac{N}{4}$ sulphuric acid) is equivalent to 0.003351 gram ammonia by the barium chloride method, and 0.003372 gram ammonia by the ammonium sulphate method, as carried out by myself. I think that as a method of standardization the ammonium sulphate method will be found very simple and accurate and for these reasons should commend itself to those analysts who make use of sulphuric acid as their standard acid.

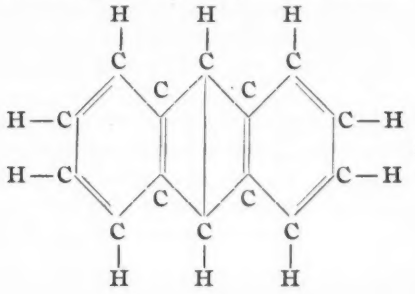
February 11, 1895.

ON SOME EXPERIMENTS IN THE ANTHRACENE SERIES.

By C. E. LINEBARGER.

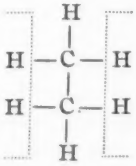
Received March 4, 1895.

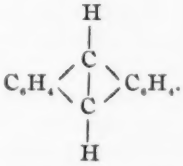
TO anthracene is generally assigned the formula:



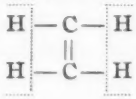
;

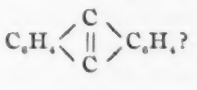
it may also be thought of as ethane, in which four of the hydrogen atoms have been replaced by the two bivalent radicals, phenylene:





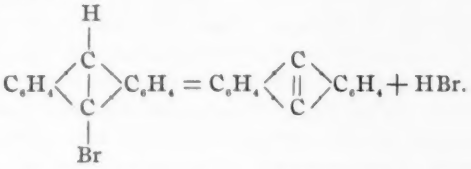
In both the formulas, the two middle atoms of carbon are bound directly together, and the hydrogen atoms in immediate union with them—in the so-called γ-position,—exhibit a characteristic behavior. The question arises, can not the γ-carbon atoms become bound together doubly, so as to form a hydrocarbon, which may be regarded as derived from ethylene,





The question appeared to possess enough importance to merit investigation, and in what follows an account is given of the experiments carried out in seeking an answer to it.

The first attempt to prepare such a compound as the above was made by a study of the action of heat upon mono-brom-anthracene. It seemed likely that through the application of heat hydrobromic acid would be formed by the combination of the hydrogen and bromine in the γ-position, and the bonds of carbon thus set free would unite with each other, as shown in this equation:



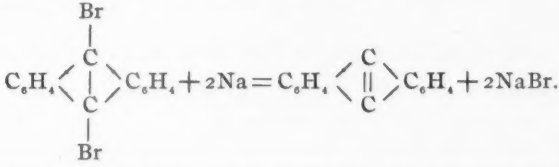
Ten grams of pure mono-brom-anthracene were heated in a small round-bottomed flask provided with a delivery-tube. The

flask was set upon a sand-bath, and its upper part protected from the direct action of the heat by means of a shield of asbestos board. A thermometer was inserted through the cork, reaching almost to the bottom of the flask, so that its bulb was completely immersed in the heated substance. Heat was applied slowly, and it was found that hydrobromic acid gas commenced to pass off at 250° C., and the evolution became quite brisk at 280° to 300°. The temperature was not, however, allowed to rise higher than 300°, and when the evolution of gas had nearly ceased, the heating was discontinued. The neck of the flask was full of yellowish crystals, while in its bottom there remained a black resinous mass from which no crystalline substance could be obtained. The crystals were dissolved in hot benzene, and the solution, on cooling, became filled with tablets resembling those of anthracene. These, by a second crystallization from a mixture of alcohol and benzene, were obtained in a state of purity. Their melting-point was found to be 210° to 212°, which is that of anthracene; they were also, like anthracene, soluble with dark green color in concentrated sulphuric acid; there is no doubt, therefore, that the product of the reaction, that is, as far as anything crystallizable is concerned, is anthracene. The hydrogen necessary for its formation must have been taken from the resinous mass.

Experiments were now carried out on the action of alcoholic potash on the brominated compound of anthracene. Three grams of mono-brom-anthracene were heated with twenty grams of alcoholic caustic potash in sealed tubes at temperatures varying from 100° to 250°. No reaction seemed to occur at temperatures below 150°; the products obtained at higher temperatures were always about the same. When the tubes, which were always filled with crystals, were opened, considerable quantities of inflammable gases escaped; the crystals, when washed free from caustic potash and purified by crystallizations from alcohol, melted at 207° to 211°. This point of fusion together with the appearance of the crystals—small glistening tablets possessing fluorescence—and the characteristic green coloration with strong sulphuric acid is sufficient evidence that the product is merely anthracene.

The action of solid caustic potash in like circumstances gave also nothing but anthracene.

An investigation was now made of the action of metallic sodium on di-brom-anthracene dissolved in different liquids. It was thought that, perhaps, the sodium would abstract the halogen from the anthracene compound, and that union would then occur between the two γ-carbon atoms, thus:



A molecule of di-brom-anthracene, together with nearly enough benzene to dissolve it, was sealed up in a tube with somewhat more than four molecules of sodium, and heated at 100° for eight hours; no reaction took place. When heated, however, for the same length of time at 125°, the contents of the tube had turned black. The tube was opened, and the dark-colored crystals purified by repeated crystallizations from mixtures of benzene and alcohol. The crystallizable product finally obtained was nothing else than di-brom-anthracene; the reaction which had supervened had evidently not effected the desired synthesis.

The reaction was now tried with xylene as solvent. Ten grams of di-brom-anthracene were dissolved in sixty grams of xylene—which had been distilled over sodium—and an excess of sodium added. The solution was kept vigorously boiling for twenty hours, an inverted condenser being used. The dark colored products of the reaction were filtered off hot, and the crystals, that soon separated out from the filtrate, repeatedly crystallized out of benzene until a pure product was obtained. This showed itself, by its melting-point (207° to 210°), fluorescence, and coloration with concentrated sulphuric acid, to be anthracene. The sodium did, indeed, remove the bromine, but so unstable a molecule was formed that a portion of the product was destroyed in order to yield hydrogen for the formation of anthracene.

The above are the simplest and most direct methods for realiz-

ing the proposed synthesis. Whether others will succeed where these have failed is an open question; at any rate the theoretical importance to be attached to the possibility of existence of such a hydrocarbon as $C_6H_4\begin{matrix}\diagup\\ \\ \diagdown\end{matrix}\begin{matrix}C\\ \|\\ C\end{matrix}\begin{matrix}\diagdown\\ \\ \diagup\end{matrix}C_6H_4$ makes it desirable that all the methods be tried.

CHICAGO, March 1, 1895.

ON THE REACTION BETWEEN ZINC SULPHATE AND POTASSIUM HYDROXIDE.[1]

BY C. E. LINEBARGER.

Received March 4, 1895.

It is customary in books on analytical chemistry to represent the precipitation of zinc hydroxide from solutions of its sulphate by means of potassium hydroxide, and its redissolution by the action of an excess of the alkali by these two equations:

(1) $ZnSO_4 + 2KOH = Zn(OH)_2 + K_2SO_4$.

(2) $Zn(OH)_2 + 2KOH = ZnO_2K_2 + 2H_2O$.

These equations are, however, far from corresponding to actuality, and it seems really deplorable that chemists in their desire to formulate compounds and balance equations should, by symbolical representations on paper, give the impression of having duly explained such a reaction as the above, which even a superficial examination shows to vary considerably with the temperature, dilution, and relative masses of the components.

The general scheme followed out in this preliminary study of the reaction of the two salts in question consisted in the addition to a constant quantity of zinc sulphate, varying quantities of potassium hydroxide, the total volume and temperature of the

[1] This investigation was begun in 1888 in the chemical laboratory of the Northwestern University at the suggestion and under the guidance of Prof. A. V. E. Young. It had been the intention to study the reaction between zinc sulphate and potassium hydroxide in a manner analogous to that in which Prof. Young had made "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydrate," published in the Proceedings of the American Academy of Sciences and Arts, June 10, 1885. Only certain preliminary experiments, however, had been performed when I left the University, and the research has not received further attention at the hands of Prof. Young or myself. While these preliminary experiments can be said to be but a small part of the work necessary for the elucidation of the problem of the chemical equilibria presented by the system of zinc sulphate, caustic potash, and water, yet they possess a certain interest, especially for analytical chemistry, which may warrant their being made known.

system being kept constant in all experiments, and the immediate analysis of the precipitate. The details were as follows: 36.2 cc. of a solution containing two grams of anhydrous zinc sulphate were brought into a graduated 500 cc. flask, and diluted to about 225 cc. The required quantity of potassium hydroxide solution was also diluted to about the same volume and added to the zinc sulphate. The flask was briskly shaken, the volume of the mixture made up accurately to 500 cc., again well shaken, so as to insure a homogeneous mixture, and the whole thrown upon a large dry filter. Portions of fifty cc. each of the filtrate were taken and analyzed, duplicate determinations being made of zinc and sulphuric acid, and in some cases of potassium. The sulphuric acid was determined volumetrically by precipitation with barium chloride according to Wildenstein's method, the zinc, volumetrically by precipitation with sodium sulphide, lead acetate in alkaline solution being used as indicator, and the potassium, gravimetrically as potassium sulphate. From the analysis of the filtrate, it is easy, since the total amounts of substances present in the system are known, to calculate the composition of the precipitates.

Before the communication of the results of these experiments, it is well to mention a couple of experiments, designed, one to find out the amount of fixed alkali necessary to just precipitate all of the zinc, the other to ascertain how much was required to redissolve the precipitate. In the first experiment, potassium hydroxide was added, from a burette, to a solution of zinc sulphate of known concentration, until the resulting solution was alkaline, care being taken that the same amount of zinc sulphate and about the same amount of water was present as in the precipitation experiments. It was found that one molecule of anhydrous zinc sulphate is precipitated by 1.62 molecules of potassium hydroxide.

In the second experiment, potassium hydroxide was added from a burette to a solution containing one molecule of anhydrous zinc sulphate until the precipitate, at first formed, redissolved, 13.2 molecules of the alkali being required. In this case, however, the dilution was somewhat different from that in the precipitation experiments.

In Table I are given the results of the experiments:

TABLE I.

I. No. of Ex.	II. Mols. KOH to one mol. $ZnSO_4$.	III. Per cent. ZnO in precipitate.
1	0.25	17.11
2	0.50	35.10
3	1.00	68.08
4	1.62	100.00
5	2.00	98.49
6	3.00	96.79
7	5.00	89.76
8	7.00	68.87
9	13.20	0.00

If these data be plotted in a curve, the axis of abscissae being the number of molecules of potassium hydroxide to one molecule of anhydrous zinc sulphate, and the axis of ordinates being the per cent. of zinc oxide in the precipitate, it is seen that the curve at first ascends almost in a straight line to ordinate = 100, and abscissa = 1.62 (the point of complete precipitation), and then falls to ordinate=0, and abscissa = 13.2 (the point of re-solution) in a perfectly regular manner.

CHEMICAL BRICK FOR GLOVER TOWERS.

BY IRVING A. BACHMAN.

Received January 15, 1895.

IN the last year, Chemical Brick for Glover Towers, from a new locality,[1] have been placed upon the market, which in physical appearance and color are like the famous Blue Welch Brick, and in quality rival them.

Specific gravity, 1.93. Hardness, 7.5.

Color, umber blue. Fracture, blue.

Silica,	SiO_2	72.11 per cent.
Alumina,	Al_2O_3	20.58 "
Iron oxide,	Fe_2O_3	5.48 "
Calcium oxide,	CaO	0.92 "
Magnesium oxide,	MgO	0.54 "

A whole brick placed in the bottom of working Glover Tower, acid at 62° B. and 310° F., lost as follows:

[1] Manufactured from the Aiken, S. C., clays.

Weight of brick									2934.22	grams.
"	"	"	at expiration of		1	week			2933.01	"
"	"	"	"	"	2	weeks			2931.92	"
"	"	"	"	"	3	"			2929.41	"
"	"	"	"	"	4	"			2928.36	"
"	"	"	"	"	5	"			2927.11	"
"	"	"	"	"	6	"			2925.26	"
"	"	"	"	"	7	"			2923.99	"
"	"	"	"	"	8	"			2922.78	"
"	"	"	"	"	9	"			2921.53	"
"	"	"	"	"	10	"			2920.05	"

Whole brick immersed in boiling

			66° B.	sulphuric	acid,	5	hours,	lost	0.08	per cent.
Same	reweighed	"	60° B.	"	"	5	"	"	0.07	"
"	"	"	50° B.	"	"	5	"	"	0.06	"
"	"	"	47° B.	"	"	10	"	"	0.06	"

A piece from interior of brick immersed in boiling

			66° B.	sulphuric	acid,	5	hours,	lost	0.15	per cent.
Same	reweighed	"	50° B.	"	"	5	"	"	0.07	"
"	"	"	50° B.	"	"	5	"	"	0.07	"
"	"	"	47° B.	"	"	5	"	"	0.04	"

The edges still remained firm and sharp.

AUGUSTA, GA., January, 1895.

THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

BY THOMAS H. NORTON.

[*Continued from page 260.*]

At about this period several processes were introduced for the preservation of wood against decay; and claims were made that these were also valuable for rendering wood uninflammable.[1] These processes consisted essentially in the introduction into the pores of wood of metallic salts in solution, which combined with the nitrogenous matter present to form insoluble, non-fermentable compounds, and therefore removed sources of decay.

The chief methods employed were kyanizing or impregnation with mercuric chloride; burnettizing or impregnation with zinc chloride, using a three per cent. solution; boucherizing or injection of copper sulphate, using a one per cent. solution; and

[1] Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, *1885*.

Beer's process of impregnating with borax. All of these methods give partial protection against combustion. With regard to their availability, expense and the evolution of poisonous vapors, when exposed to heat, militate against the use of corrosive sublimate. Copper sulphate, which can be absorbed to the extent of twenty kgms. per cubic meter of wood, is far inferior to many other salts as a fire protective; it colors the wood blue when exposed to atmospheric conditions, and in common with the mercuric salt, corrodes iron nails and bolts. Zinc chloride is more efficient, although in common with the two preceding salts it affects the tenacity and elasticity of wood. Borax seems to be more free from the objectionable features just enumerated, and more recent experiments have shown that its protective power is far superior to that of the copper or zinc salts, although inferior to that of sodium tungstate and ammoniacal salts.

The operation of impregnation in closed vessels by the use of a vacuum was devised by Samuel Bentham in 1794. It was successfully employed in France by Bréant and Bethel in 1830, and later in England for the purpose of kyanizing and burnettizing, as well as in connection with Payne's process.[1] In boucherizing, the copper sulphate solution is usually forced longitudinally from the butt to the trunk of a tree, just after it is felled, by an ingenious arrangement, involving the use of rubber caps and an elevated tank.[2]

In 1855 Salomon's process[3] of treatment with aluminum sulphate and calcium chloride, already described in connection with textile fabrics (p. 147) was applied to wood with some little success.

During this same year Maugham's process[3] of treating wood with a mixture of sodium phosphate and ammonium chloride, and Jackson's process, based on the combined use of zinc and ammonium salts, were both submitted to critical tests by Sir Frederick Abel,[3] who found neither as cheap or as efficient as sodium silicate. Abel reported at length to the English Board of Ordnance on the advantages offered by the use of sodium silicate, which he had recommended at an earlier date for use in the

[1] Frémy, *Dict. de Chimie*, 10.
[2] Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, *1885*.
[3] Amer. Arch., loc. cit.

tenths, one, two, three and five-tenths, five, ten, fifteen, and twenty per cent. solutions of the anhydrous compound. After being hung on lines and drying at ordinary temperature, the lower ends, where greater quantities accumulate, are clipped off. When insoluble precipitates are to be obtained in the paper, it is first soaked in a solution of the soluble salt, then dried, then soaked in a solution of the precipitating reagent, dried, washed, soaked for six to twelve hours in water, washed, and finally dried. The strips are then folded lengthwise, and while held horizontally, with the folds beneath, kindled at one end. Observation then shows whether the foreign substance hinders or helps combustion, and what is the minimal relative weight of a salt or the minimal strength of its solution, necessary to render the paper uninflammable.[1]

Experiment indicates that different substances, although in solutions of equal strength, are retained unequally by the paper; the amount retained increasing in proportion to the insolubility or ease of crystallization of a compound. Very soluble substances are absorbed in almost equal proportions. It is also worthy of note that apart from compounds which are practically storehouses of oxygen, as the chlorates, there are substances which distinctly favor combustion, the alkaline sulphates for example. As illustrations of Lochtin's method, a strip soaked in a twenty per cent. solution of sodium sulphate is kindled at one end. It is observed that it burns easily and readily to the end, as readily as if no foreign matter were present. Again, four strips of paper soaked in ammonium chloride solutions, *a* in a twenty per cent. solution, *b* in a five per cent. solution, *c* in a two per cent. solution, and *d* in a one per cent. solution, are in turn held in the flame. No propagation of flame is shown by *a*; *b* shows a small flame, which is extinguished quickly on removal from the source of heat; *c* yields a larger flame, which burns for about five cm. after removal; and *d* furnishes a still larger flame, which burns to the end. It is evident that the use of a two per cent. solution affords partial protection, and of a five per cent. solution, full protection against inflammability. I have found in personal experience an advantage in using for elementary tests the thin slips of pine wood about eight cm. long and one cm. wide, easily

[1] *Dingler's Poly. Jour.*, 290, 230.

obtained from any tobacconist. These are preferable to Lochtin's strips, as they can be used for testing protective coverings as well as solutions; and in the case of the latter the distribution of the foreign substance throughout the strip is more uniform. The experiments conducted before you, illustrate the relative resistance imparted by a number of the preparations already enumerated.

A third method of comparative testing was devised by Boudin and Donny.[1] A cylinder of light iron rods forty cm. long and twenty-five cm. in diameter is mounted upon an horizontal axis so that it can be easily kept in rotation. Beneath this cylinder is a series of five Bunsen burners, consuming 1000 liters of gas hourly. The wood used for the experiments is in the form of rectangular sticks thirty-nine cm. long and fifteen mm. square. After treatment by injection or painting, bundles of four sticks of each preparation—the individual sticks kept apart by light wedges—are attached by wire to the rods of the cylinder, parallel to its axis, and at equal distances from each other. A bundle of sticks which have not been treated serves as point of comparison in each charge of the cylinder. The row of lamps is next lighted, and the cylinder turned at the rate of six revolutions per minute, so that all of the bundles are uniformly and evenly exposed to the action of the flame. The time is then noted at which each bundle takes fire, or is seriously affected by the heat; and when the combustion of a bundle becomes sufficiently active to affect its neighbors, it is removed. As an example of the working of this method the following series of tests may be quoted from the Belgian report:

Wood not treated took fire at the end of one and three-fourths minutes.

Wood treated with zinc sulphate or alum, at the end of three and one-half minutes.

Wood treated with ammonium sulphate or copper sulphate at the end of five minutes.

Wood treated with borax, or boric acid, or Martin's ignifuge, or Brocher's preparation, at the end of eight minutes.

[1] Rapport.

Wood treated with sodium tungstate, at the end of ten minutes.

Wood treated with calcium chloride or ammonium chloride, at the end of fifteen minutes.

Wood treated with waterglass alone, or with lime, or with powdered glass and kaolin, or cyanite, or the Bell, Blane, or United Asbestos Co. preparations, or ammonium phosphate, at the end of thirty to forty minutes.

The two latter were charred throughout without the production of flame.

A still more rigorous and decisive test has been devised by Boudin and Donny,[1] one which places the experimenter as nearly as possible in the conditions which ordinarily precede the outburst of a conflagration; *viz.*, the production of a flame of greater or less intensity in immediate contact with inflammable material; such as happens when an oil lamp is overturned, a box of matches is kindled by the gnawing of an inquisitive rat, or the like.

The test is simple in its nature, and depends, as in the preceding method, upon the use of wooden rods subjected to a protective treatment. A convenient size is that of twenty cm. in length and fifteen mm. square. Thirty-six rods of the same preparation are used to form a small open construction by simply superimposing rows of six alternately crossed upon each other, leaving in the center an open space about six cm. wide for the reception of burning material. The whole arrangement is one permitting of the freest possible circulation of air, a condition which is further aided by placing the construction upon a piece of heavy wire gauze, supported upon two bricks. Little bundles of splints, weighing thirty-five grams each, are used as sources of combustion. They are introduced into the central space, lighted, and the result carefully noted. If combustion be not communicated to the construction by the burning of a single charge, a second is added, and so on. It is easily seen from the series of experiments with these constructions carried on before you, that this method of the two Belgian chemists is of the most searching and exacting nature, and yields comparative results of the highest value.

[1] Rapport.

In such a series of tests, for example, a construction of ordinary wood takes fire at the end of one minute, is in complete combustion two minutes later, and at the end of ten minutes leaves a mass of ashes. Wood treated with ammonium chloride takes fire at the end of three minutes and undergoes complete combustion. Wood covered with cyanite takes fire at the end of three minutes and burns slowly for fifteen minutes, leaving the exterior intact. Wood treated with three coats of waterglass stands exposure to four successive charges of combustible, with but little evidence of the propagation of fire, although the surface of the rods is deeply altered by the exudation and swelling of the silicate. Wood treated with ammonium phosphate, or the United Asbestos Co. preparation, is scarcely affected after four successive charges. The construction remains intact with the interior slightly charred.

RESULTS THUS FAR ATTAINED.

Leaving the methods of testing, let us now briefly summarize the results of experiment, and experience with fire protectives up to the present date. For textile fabrics, sodium tungstate and magnesium borate yield, unquestionably, the best results, when materials are to be ironed, while ammonium phosphate or sulphate is preferably used in other cases.[1]

The use of the tungstate, especially, is widespread in England. It may be of interest to know that in the laundry of the Queen's palace, all fabrics of vegetable origin are treated with a solution of neutral sodium tungstate of 28° Tw. containing three per cent. of sodium phosphate. This solution is added to the starch also when the latter is employed.

Abel's researches[2] show that in naval warfare, calcium chloride is valuable to protect rope mantelets, while canvas is well protected by stannic oxide and still better by the double silicate of sodium and lead.

The efficacy of sodium tungstate, as well as of the ammonium salts, for the scenery and decoration of theaters, has also been firmly established.

The comparative results of Lochtin's experiments on pure cel-

[1] F. Fischer, *Ding. Poly. Jour.*, 245, 36.
[2] Amer. Arch., 13 and 14.

Crimea to render huts fireproof, and which was used in 1856 in camp huts at Aldershot for the Royal Engineers. By applying first a coat of silicate, then a coat of lime, and finally a second coat of silicate, Abel obtained a covering which resisted rain and showed no tendency to crack, shrink, or detach itself from the wood. The cost was one cent for five square feet. Later reports to the board made by Abel in 1870 and 1872 state that the efficiency of this protective was totally unaffected by time. In 1881 he also reports that sodium tungstate, already employed for fabrics, may be successfully used for wood, but that it offers no advantages over the sodium silicate process. It is absorbed by wood at the rate of fifty-six kgms. per cubic meter.

Patera, who studied the subject very extensively, recommended in 1871,[1] the use of magnesium borate for wood, finding it fully equal to sodium tungstate. He urged also very strongly the use of a mixture of one part strong ammonia and two parts gypsum, especially for roofing. Severe tests applied to this protective yielded such satisfactory results that the Austrian Minister of Finance recommended it for all government buildings where woodwork was exposed. Patera also advises the use of a coating of one part of ammonium sulphate, two parts gypsum, and three parts water. Another protective covering recommended by him is obtained by first coating wood twice with a saturated solution of three parts of alum and one part of copperas, and then applying a coat of clay mixed in copperas solution.

The successful use of sodium silicate led to the employment of various siliceous paints. One devised by Vilde and Schambeck[2] seems to have given good results. Its composition is pulverized glass twenty parts, pulverized porcelain twenty parts, pulverized stone twenty parts, quicklime ten parts, waterglass thirty parts. The thick syrup is applied with a brush and hardens quickly.

Ransome's siliceous paint,[3] introduced in 1871, consisted of a mixture of pure quartz and waterglass. After application it was coated with calcium chloride in order to render it perfectly insoluble. It has not been used of late years.

Another process involves the application of three coats of dilute

[1] Loc. cit.
[2] Sc. Amer. Cyclop. of Receipts, p. 217.
[3] Amer. Arch., loc. cit.

waterglass, then of two coats of the same mixed with powdered glass; finally of one of thick waterglass.[1] Other preparations consist simply of more or less dilute waterglass, to which zinc oxide or ferric oxide has been added.[1] A most important modification of the simple silicate is that known as cyanite[1] and prepared by introducing aluminum hydroxide into waterglass, so that it is practically a basic aluminum silicate. It is a perfectly colorless liquid, and is applied with a brush. The cyanite is manufactured in England, and is employed in the English War Department by the Woolwich Arsenal, and by the Department of Railroad Inspection. That the product is variable would be indicated by Helbig's analysis[2] in 1888, when he found nothing present but waterglass.

Among other recent preparations is the ignifuge of Martin[3] of France (1880) used for impregnation, and composed of ammonium chloride fifteen parts, boric acid six parts, borax three parts, water 100 parts.[1] Another French preparation is that of Vendt and Herard,[4] 1885, also for impregnation. It consists of alum twelve parts, borax five parts, sodium thiosulphate three parts, potassium sulphate ten parts, water seventy parts. Somewhat peculiar are the following combinations, also used in France;[5] the first a solution of lead sulphate in neutral tartrates; the second an ammoniacal solution of a mixture of calcium acetate and calcium chloride. Brocher's preparation,[1] manufactured near Dresden, and used to some extent in Germany, is of unknown composition, and involves the use of three different liquids in the course of the application of the several coats. Objection has been made to it for this reason, as well as on account of the tendency of the solutions to solidify before use.

The general recognition of the utility of protective coatings led gradually to the extended use of asbestos. E. G. Erichsen,[6] of Copenhagen, in 1881, devised a new protective which consisted of a soluble silicate, metallic oxides, and lime, with ten to twenty

[1] Boudin et Donny, Rapport.

[2] Archiv. f. Hygien, *1888*, III.

[3] Troost, *Bull. de la Soc. d'Encouragement*, *1880*, p. 384.

[4] *Génie civ.*, 6, 227.

[5] Frémy, *Dict. de Chimie*, 10.

[6] Amer. Arch., loc. cit.

per cent. of asbestos. It was applied with a trowel and formed a sort of fire-proof enamel which could be washed with water. Erichsen's preparation was extensively used in Europe, both on the continent and in England.

A further step forward was made in 1883, by C. J. Mountford,[1] of Birmingham, England, who brought out a preparation which consisted of asbestos ground and reground in water, sodium or potassium aluminate and waterglass. When liable to exposure to atmospheric agencies, it receives, further, a certain amount of oil driers and gummy matters and sometimes zinc oxide or barium sulphate. The United Asbestos Co., of England, has manufactured this product on a large scale for ten years, and it has been extensively employed, especially in England. Among other important edifices treated with it are the Parliament Buildings, the British Museum, South Kensington Museum, the Crystal Palace, various theaters, Royal palaces, etc. The cost of this material is eighteen cents per kilogram, and 100 kgms. suffice to cover, with three coats, a surface of fifty-four square meters, so that the cost per square meter is about thirty-three cents. It is a thick, gray product, easily applied, presents a satisfactory appearance when used alone on wood, and furnishes an excellent basis for the application of other paints.[2]

This represents probably the best type of protective coating, thus far devised. There are also two other English preparations of some repute, the nature of which is apparently analogous to the above; Bell's asbestos paint and Blane's fire-proof and water-proof paint;[2] while, in America, a single firm manufactures an asbestos paint.

Such is the history of the different methods of restricting the combustion of wood which have been presented during this century.

Let us next note the means devised to test comparatively the value of the diverse materials recommended.

TESTS FOR FIRE-PROOF PREPARATIONS.

In Versmann and Oppenheim's extended investigation on protectives for textiles,[3] the study was carried on in such a way as

[1] Amer. Arch., loc. cit.
[2] Boudin et Donny, Rapport.
[3] Report to the British Association, *1859*.

effectually to eliminate one after another of the salts experimented upon until a small group was left, the efficiency of each member of which, under varying conditions, was satisfactorily demonstrated. The usefulness of impregnation by sodium tungstate is easily illustrated by exposure to a flame of strips of cotton cloth, some of which have been soaked in a tungstate solution, while others are in the ordinary condition. The merits of the different protectives for wood, as each one in turn came before the public, until a recent date were usually tested by application to a small hut or the like, within which an active fire of very combustible material was started. Such was the custom of Sir Frederick Abel[1] in his series of experiments already referred to.

Some thirty years ago Professor Pepper, of London, made comparative tests on four salts, strongly recommended for impregnating wood, and as a result placed them in the following order, the most efficient first:[2]

1. Ammonium phosphate.
2. Sodium tungstate.
3. Borax.
4. Alum.

The most thorough and valuable study in this field was made in 1887 by two Belgian chemists, Professors Boudin and Donny, of the University of Gand (Ghent) at the request of the Belgian Minister of Public Works.[3] They submitted to rigorous comparative tests all of the preparations then in vogue, some nineteen in number, and it is to be regretted that their exhaustive report has not been reproduced *in toto* in our journals.

P. Lochtin,[4] in 1893, introduced a simple and easy, if not perfectly exact method of testing, which he applied to about fifty chemical compounds, and brought out several interesting facts.

We will consider first his more elementary methods, taking up later the more improved ones of Boudin and Donny.

Lochtin used strips of thick filter-paper fifty cm. long and five cm. broad, which are soaked in solutions of the substances submitted to experiment, usually a series for each substance of five-

[1] Amer. Arch., loc. cit.
[2] Sc. Amer. Cyclop. of Receipts, p. 217.
[3] Rapport sur les procédés destinés á assurer l'ininflammabilité des bois, Gand, *1887*.
[4] *Dingler's poly. Jour.*, 290, 230.

lulose[1] may well be summarized here as they offer a valuable classification and furnish useful hints; although it must not be forgotten that the tests were elementary in their nature, and the conclusions, hence, open to criticism, as is, in some cases, evident.

Lochtin divides compounds into three classes, with reference to the effects on combustibles. (1) The *antipyrenes*, which render cellulose uninflammable when present in relatively small amounts, and when used in weak solutions. (2) *Indifferent substances* which are effective only when present in large amounts. (3) *Substances which favor combustion.*

I. ANTIPYRENES.

Quantities of anhydrous substances required to render cellulose uninflammable.

	Minimal strength of solution used in per cent.	Minimal relative weight (cellulose = 100).
NH_4Cl	1.5	4.2
$(NH_4)_2HPO_4$	1.5	4.5
$(NH_4)_2SO_4$	1.5	4.5
$ZnCl_2$	1.5	4.0
$CaCl_2$	1.5	4.5
$MgCl_2$	1.5	4.5
$Al_2(OH)_6$	1.5	3.8
$KAl(SO_4)_2$	2.0	..
$ZnSO_4$	1.5	4.5
$SnCl_2$	2.5	..
$Na_2B_4O_7$	1.5	8.5
B_2O_3	2.5	10.0

II. INDIFFERENT SUBSTANCES.

HKO	7.5	..
$MgSO_4$	7.5	15
NaCl	7.5	35
Na_2SiO_3	17.5	50
SiO_2	12.5	30
KCl	20.0	45
Na_2HPO_4	7.5	30
K_2HPO_4	20.0	..
$Al_23(B_4O_7)$	12.5	24
$AlPO_4$	10.0	30
$Ca_32(PO_4)$	12.5	30
$MgHPO_4$	12.5	30
ZnB_4O_7	7.5	20
$ZnHPO_4$	15+	..
WO_3	10+	15+
Na_2WO_4	10+	15+
$(NH_4)_2WO_4$	7.5	10+
Clay (air dry)	..	75
$NaC_2H_3O_2$ and $KC_2H_3O_2$	7.5—5	..

[1] *Ding. poly. Jour.*, 290, 230.

III. SUBSTANCES FAVORING COMBUSTION.

Na_2SO_4, Na_2SO_3, Na_2CO_3, Na_2SnO_3, $Mg(OH)_2$, K_2SO_4, $ZnCO_3$, $CaCO_3$, $MgCO_3$, $CaSO_4$, $FeSO_4$.

In reviewing the above tables, it is of importance to note that the aluminum hydroxide used is that obtained by double decomposition between sodium aluminate and sodium bicarbonate. The product formed by the action of ammonia on aluminum sulphate is of no value. It will be seen, also, that the somewhat expensive sodium tungstate is much less effective than many other compounds, the chemical nature of which debars them, however, from ordinary application. Thus, (apart from cost), acid or alkaline reaction, difficulty in solution, hygroscopic properties, or readiness to decompose, on contact with hot iron or otherwise, handicap, as it were, most of the antipyrenes. The chief value of Lochtin's work is to be found in the recognition of aluminum hydroxide as so pronounced an antipyrene and the fixing of the conditions under which it is deposited in the most effective form.

The most important and decisive results with regard to the efficiency of the different current protectives of wood are furnished by Boudin and Donny.[1] Using a classification based upon their rigorous and conclusive tests, we can arrange the protectives in the following series, ascending from the least effective to the most effective.

I. PREPARATIONS OF LITTLE VALUE.

1. Injection of sodium tungstate (56 kgms. per m^3).
2. " " copper sulphate 20 " "
3. " " calcium chloride 50 " "
4. " of ammonium chloride 48 " "
5. Coating of waterglass (43 per cent. solid residue), 1 coat, 286 grams per m^2.
6. Coating of waterglass and zinc oxide, 4 coats, 1 kgm. per m^2.
7. " " Martin's ignifuge, No. 4, 2 coats, 450 grams per m^2.
8. " " Brocher's preparation, 3 "
9. " " Blane's asbestos paint, 2 " 1 kgm. per m^2.
10. " " cyanite (basic aluminum silicate), 2 coats, 450 grams per m^2.

[1] Rapport.

II. PREPARATIONS OF SOME VALUE WHICH LESSEN, IN A MARKED DEGREE, THE INFLAMMABILITY OF WOOD.

11. Covering of cyanite, 3 coats, 570 grams per m^2.
12. " Bell's asbestos paint, 3 coats, 820 grams per m^2.
13. " waterglass[1] and ferric oxide, 4 coats, 700 grams per m^2.
14. Covering of waterglass[1] and powdered glass, 6 coats, 900 grams per m^2.
15. Covering of waterglass[1] (undiluted),[2] 3 coats, 475 grams per m^2.

III. PREPARATIONS OF THE HIGHEST EFFICIENCY WHICH PREVENT ALMOST ENTIRELY THE PROPAGATION OF FIRE IN WOOD.

16. Covering of the United Asbestos Co. paint (waterglass, sodium aluminate and asbestos), 3 coats, 850 grams per m^2.
17. Injection of ammonium phosphate, absorption of 75 kgms. per m^3 after boiling for twelve hours in a sixteen per cent. solution of the salt.

These two protectives would seem therefore the high-water mark of what chemists have attained in their efforts to render wood inflammable. With regard to the permanence of their protective power, it has been observed that, after the lapse of two years, wood treated with the asbestos preparation had lost, in no measure, its resistant qualities, while that injected with ammonium phosphate showed an exceedingly slight diminution in the efficiency. No diminution was noticed at the end of nine months in the resistance of injected wood, kept at ordinary temperature, or at 45° C., or covered with a coat of oil-paint. It should be noted also that the solution of ammonium phosphate does not affect nails and other objects in iron even after contact for several months; also that the solutions of the salt must be nearly saturated in order to yield satisfactory results.

Boudin and Donny's experiments would tend to indicate a

[1] In all these tests a waterglass of forty-three per cent. solid residue was used. It was generally diluted with water, but this additional water is not included in the weight per m^2.

[2] Wood, when first covered with waterglass, presents a varnished appearance. This is not retained long, as the coating soon begins to scale, and the surface is covered with a white efflorescence.

slight lessening in the strength of wood which has been injected. The general conclusions drawn from their investigations are:

1. The incombustibility of wood, *i. e.*, its non-alteration when under the influence of heat, cannot be attained. It is possible, however, to secure its non-inflammability, so as to preserve ordinarily any structure exposed to an accidental fire, or at least to allow time for the arrival of the ordinary extinguishing appliances, unless it be filled with combustible material.

2. Of the preservative processes used, injection of saline solutions or the application of protective coverings, the former would seem ill adapted for timber of large dimensions, but of manifest value for the less bulky forms of wood. In all such cases the use of ammonium phosphate, in saturated solution, offers such incontestable advantages, that, despite its high price, it should be employed unless excluded absolutely by limitations of expense. (Ammonium phosphate can be obtained for about $50 per 100 kgms., and as a cubic meter of wood absorbs seventy-five kgms., the cost per cubic meter would be about $38.)

3. In the majority of cases protective coatings are preferable. The most efficacious is that containing sodium aluminate and asbestos in waterglass, while waterglass alone, or with the addition of aluminum hydroxide, is of great value.

EXPLANATION OF THE ACTION OF PROTECTIVES.

Such being the practical results attained, it is of interest for us next to know in just what way these chemical compounds act to prevent inflammability. It is, in fact, a matter of surprise that the experimentation in this field has been so largely empirical, neither preceded nor followed by theoretical considerations.

In studying the effects of heat on ordinary wood, the following will be noted:[1] When exposed for some time to a temperature of 200° C., wood becomes light brown and its strength is materially affected. At 300° it is charred completely, losing all power of resistance, but still without a trace of flame. If, however, the wood be in contact with flame, or be exposed to a red heat, change takes place rapidly, and if air have free access it bursts into flame, and combustion does not cease until the entire mass be reduced to ashes.

[1] F. Fischer, *Ding. poly. Jour.*, 245, 36; Boudin et Donny, Rapport.

When wood protected by a suitable coating, such as water-glass, is exposed to a temperature of 200° C., it acts exactly as ordinary wood. Wood, however, which has been injected with saline solutions, as ammonium phosphate, is more liable to change. It assumes a deep brown tint, and the resistance to strain is greatly lessened. At 300° all forms of protected wood are carbonized, exactly as the ordinary wood, and without flame.

At a red heat, or in contact with flame, prepared wood is completely destroyed; but there is a vast difference between its rate of destruction and that of non-protected wood. At first there is a pronounced period of direct resistance. In cases where external applications have been made, the heat gradually penetrates the protective coating, jets of gas issue through fissures in it, and their combustion contributes to the intensity of the surrounding sources of heat, until, finally, combustion is complete. In the case of wood impregnated with suitable saline solutions, resistance to the flame is likewise marked, but much gas is evolved. This gas is not inflammable but seems, on the contrary, to interfere seriously with the combustion of the surrounding fire. Complete charring is finally reached. It is evident in both cases that the ordinary effects of heat upon wood are seriously hindered or retarded. The first effect of heat, as we have seen, is to produce gas and leave carbon. This gas, if allowed to burn with the oxygen of the air, furnishes a fresh supply of heat to bring about further evolution of gas. But as organic matter and the resultant charcoal are both poor conductors of heat, gasification would proceed very slowly unless the coal on the surface also changed to gas by burning with atmospheric oxygen (as well as by reducing the carbon dioxide and water present), thereby increasing the available temperature. The maintenance of a sufficiently high surrounding temperature must eventually cause the penetration of enough heat into the body of wood exposed to produce complete gasification and carbonization, and finally complete combustion of the charcoal. This action can be retarded evidently by two distinct agencies. The first is the evolution of an inert or non-combustible gas or vapor from the wood through the influence of heat; the second is the presence of an external coating, which is not only a poor

conductor of heat, but also protects the outside zone of charcoal from contact with atmospheric oxygen. It is in one or both directions that fire protectives render service.

The ammonium salts are good types of the first class. Ammonium chloride and ammonium sulphate are readily vaporized and dissociate, the first into ammonia and hydrochloric acid, the second into ammonia, nitrogen, water, ammonium, sulphite, etc. Ammonium phosphate decomposes slowly to metaphosphoric acid (sixty-two per cent. of its weight), ammonia, and nitrogen monoxide. It is probably this slowness of decomposition which renders the phosphate superior to the other ammonium salts. In the case of magnesium chloride, zinc chloride, etc., hydrochloric acid is driven off. In the case of other salts, such as the alums, the borates, copper sulphate, and sodium tungstate, large amounts of water of crystallization are necessarily liberated in the form of aqueous vapor. It is a matter of surprise that this fact, that the storage of considerable amounts of water in the solid form in the interior of wood is a potent factor in the protective value of a number of antipyrenes, should have escaped the attention of chemists. It is an easy matter to calculate the volume of aqueous vapor capable of being formed from a given weight of $Na_2B_4O_7 + 10H_2O$ or $Na_2W_4O_{13} + 10H_2O$ or $K_2Al_2(SO_4)_4 + 24H_2O$. There is no question but that such salts, as the above, retard the attack of flame chiefly through this agency at first, although after the expulsion of the water of crystallization, the presence of the saline substance coating the charred surface and acting as a poor conductor of heat, as well as preventing the access of oxygen, continues the protection for a certain time. It is in the varying ability of different compounds to form coherent, continuous protective coatings after exposure to heat that we find the reason of the superiority of one composition, for external application, over another. Thus, waterglass alone gives good results. When wood treated with it is heated, we notice a puffing out and swelling, a certain amount of vapor escapes, and the residue is left as a light, voluminous, fairly coherent covering, through which air can penetrate but slowly to the charred surface beneath, and heat is likewise conducted but slowly. The addition of aluminum

hydroxide to the waterglass seems to increase the resistant properties of this envelope, while the further addition of asbestos and the substitution of sodium aluminate for aluminum hydroxide, forming thereby practically a quadruple silicate of sodium, magnesium, calcium, and aluminum, give the highest resistant power.

It may be pertinently inquired, why does the presence of some salts seem apparently to help combustion? Lochtin explains this action[1] by the uneven distribution of some substances during drying or precipitation, more, proportionately, remaining on the surface of the paper or wood used. Here they form porous but slightly compact crusts; and these favor continued glowing or combustion by preventing a loss of heat.

PRACTICAL APPLICATION OF THE KNOWLEDGE GAINED.

With this exposition of the results attained in the contest with fire—the fruit almost exclusively of the work of European chemists—what should be the practical application of the knowledge gained to our own conditions in America? It is evident that there should be a rigorous insistence on the use of protective agencies for *all* wood employed in buildings containing material of permanent value, such as deposits of archives, museums, libraries, etc. Equally rigorous should be the requirement in the construction of exhibition buildings; of churches, theaters, and all structures wherein large assemblages are held; of the stands about our fields for athletic amusements; of cars and craft for transportation by land or water; and above all, of the edifices of our institutions of learning.

The applications enumerated above are nearly all easily within the reach of legislative enactment, as they affect the interests or lives of the public.

How far the use of protective agents may be introduced into ordinary construction, and into household equipment it is difficult to say.[2] In England the custom of protecting wearing apparel of vegetable fiber is widespread. No reason exists why American women, earnest in reform, should not advocate a

[1] *Ding. poly. Jour.*, 290, 230.
[2] *Ding. poly. Jour.*, 245, 36.

similar custom here. There is no question, however, but that great stress should be laid upon the wisdom of impregnating the curtains, draperies, and hangings of our homes.

It is to be hoped that the slow burning principle may soon be extended to domestic architecture, but even with our present methods, it is easily possible with the outlay of a few per cent. on the cost of the house to lessen enormously its fire risk. All beams, joists, studding, etc., which are later to be hidden, can be coated during the process of erection. Siliceous coatings can also be applied to all surfaces outside and inside which are ultimately to be painted. Finally, woods to be used for interior finish can be protected by steeping in a solution, preferably of ammonium phosphate, if not of one of the cheaper antipyrenes, before being varnished. Such a house, if isolated, and presupposing the use of wire lath, is practically fireproof in nineteen out of twenty cases of ordinary conflagration. If provided with brick walls and slate roof, the risk is greatly lessened, and it is not difficult to recognize that blocks or districts of such construction are free from *all* danger of conflagration: that, in fact, fire will be confined exclusively to such rooms or houses as may be used for the storage of combustible material. Insurance, under such conditions, approaches almost the vanishing-point; and the freedom of apprehension from loss by fire is not to be measured by dollars and cents. We are here entering upon the proper province of another science. The chemist has provided the means of coping successfully with the dangers of combustion. It is for the economist to insist on the utilization of his achievements, in assuring increased comfort and security to society. Suffice it only to add that existing structures may, to a great extent, be protected especially for those few precious minutes between the discovery of a fire and the arrival of aid, by the generous application of the siliceous compositions to all exposed woodwork. The direct value of such treatment has been promptly recognized in England by a decrease of fifty per cent. in the insurance rates on houses so treated.

FIELD FOR FURTHER INVESTIGATION.

Finally, what remains for the chemist to do in this field?

Indirectly he may accomplish much in lessening the fire risk. First in the study of illuminants. Whatever tends to displace the use of petroleum for domestic lighting tends, by so much, to diminish the national fire bill, as this one substance is a most prolific cause of conflagration. It is to be hoped that the way may be opened to an economical and convenient use in this connection of our vegetable oils, now so abundant; or to the introduction of a fuel-gas saturated with hydrocarbons, so safe and economical that it may be promptly accepted for domestic lighting. The possibilities offered in this direction by the extended utilization of calcium acetylide are also most hopeful. Next there is little doubt but that the early approach of the era of cheap aluminum will effect an important revolution in the use of structural materials, the light, unchangeable metal tending to displace wood in many of its external and internal applications. In this field American chemists have taken the lead.

With regard to the production of new protectives it is hardly probable that the last word has been said. We have seen how experiment, beginning with sodium silicate, led successively to the addition of aluminum hydroxide, of lime, of lead salts, of powdered glass, and of finely divided asbestos to the convenient syrupy medium. There is but little doubt that other combinations, less expensive or more effective than those now in vogue, await the experimenter.

The high rank of aluminum hydroxide among protectives, as shown by Lochtin, should lead to extended research with regard to its availability under different conditions, and its most economical application.

The utility of magnesium borate, so warmly recommended by Patera and Fischer, should be definitely established by comparative tests. It is not unlikely that combinations of the borates and silicates may also be found to render good service. Experiments on the deposition of insoluble tungstate in fabrics are also worthy of being carried out.

With regard to protection, by impregnation, it is doubtful whether any better agency than ammonium phosphate can be

found. It would, however, be advisable to study the economical production of this salt for the purpose in question. Might it not be possible to attain cheapness by using successive baths of ammonium sulphate and sodium phosphate; or could not acid calcium phosphate be brought advantageously into the reaction?

A further field of investigation is the possible combination of injection and painting, impregnation with such deliquescent chlorides, as zinc chloride, or magnesium chloride, being followed by a simple external coat of a siliceous paint. Then the most favorable time for injecting or steeping wood with saline solutions should be definitely ascertained. Is it, after completed seasoning, or when the wood is perfectly green, as advocated by Jones?

The question of the most economical combination of protection against fire and of preservation from decay and insect attack, remains also to be settled.[1] Another important phase is the highest attainable efficiency, from the use of salts which store up, in wood, considerable amounts of water of crystallization, such as gypsum; for it must be borne in mind that every volume of solid water of crystallization yields 1700 volumes of aqueous vapor at 100° C.

It is largely along these lines that we may expect to see advance made in the province whose survey we now complete.

In conclusion, let me express the earnest hope that individually and collectively the influence of this Association may be helpfully thrown in favor of any general effort to lessen our tribute to fire. We have made ourselves felt in movements to combat the twin, although antithetic, evils of drought and flood by the preservation and extension of our forests, as well as in other economic directions. Can we not do the same in availing ourselves of the work of Gay Lussac, Fuchs, Versmann, Oppenheim, Abel, Tessier, Patera, and other chemists, by bringing into the American home and the American community that peaceful security and liberation from a dreaded tax, which comes with the practical abolition of danger from conflagration?

[1] Rymer-Jones, *Ecl. Eng. Mag.*, **33**, 55, *1885*.

A STUDY OF THE CHEMICAL BEHAVIOR OF TUNGSTEN AND MOLYBDENUM AND THEIR TRIOXIDES[1].

By Charles Hatch Ehrenfeld.

Received March 2, 1895.

INTRODUCTION.

Group VI of the Periodic System contains a sub-group of more metallic elements—chromium, molybdenum, tungsten, uranium—among the derivatives of which many interesting analogies manifest themselves. Upon comparing the metals themselves, numerous points of interest appear. Thus, beginning with chromium, possessing the lowest atomic mass as well as the highest specific heat, we observe that it oxidizes but slowly when heated in ordinary air. Molybdenum gradually changes under like conditions through its brown and blue oxides until finally it reaches its most stable form, molybdenum trioxide. The same may be remarked of tungsten, although it burns only at elevated temperatures. Uranium, on the contrary, oxidizes at relatively low temperatures. Considering this sub-group as a whole, we can probably detect greater similarities in chemical deportment and analogies in derivatives between molybdenum and tungsten than between the remaining members. To learn more of the behavior of these two metals, to disclose, if possible, differences of conduct while exposed to the influence of the same reagents, is the chief aim of the present investigation. Prefacing the actual study of the metals are some observations upon the deportment of their trioxides which are not devoid of interest, especially as they, in a measure, confirm some earlier observations. The results of this research, while largely of a qualitative character, yet demonstrate quantitative differences between tungsten and molybdenum which serve to define more clearly their position in the Periodic System.

I. *Action of Phosphorus Pentachloride upon Tungsten and Molybdenum Trioxides.*—Persoz and Bloch (*Compt. rend.*, **28**, 86, 389) assert that if the anhydrides of inorganic acids be heated

[1] From author's thesis presented to the Faculty of the Department of Philosophy of the Univ. of Pa. for the degree of Ph.D., 1894.

together with phosphorus pentachloride, the products of the reaction will consist of the anhydride and phosphorus pentachloride. They say, for example, that under this treatment tungsten trioxide yields the derivative $WO_3.PCl_5$. Hugo Schiff (*Annalen der Chemie*, 102, Heft I) expresses the opinion that in the reaction described, the final products are compounds of equivalent amounts of phosphorus oxychloride with the chlorides of the acids; that tungsten trioxide and phosphorus pentachloride yield a reddish-brown liquid, from which phosphorus oxychloride can readily be distilled, leaving at the same time a reddish-brown residue. The latter, Schiff believes to be tungstyl (or wolframyl) chloride, WO_2Cl_2.

Teclu has made a more recent investigation of this reaction (*Annalen der Chemie*, **187**, 255). He finds that as a result of heating tungsten trioxide together with phosphorus pentachloride to 170° in a sealed tube, he obtained tungsten *hexachloride*. Its solution in phosphorus oxychloride was brown in color.

It seemed to me while engaged in a study of the behavior of tungsten trioxide in vapors of various gaseous compounds, that a repetition of this experiment of Teclu was quite desirable. To this end, equivalent weights of tungsten trioxide and phosphorus pentachloride were intimately mixed, introduced into a porcelain boat, and the latter placed in a hard glass tube contracted at intervals. The air in the tube was expelled by conducting carbon dioxide through it. On applying heat to the boat a white and very volatile crystalline sublimate made its appearance. This was caught at the extreme anterior portion of the tube. Vapors of phosphorus oxychloride were given off, recognizable by their characteristic sharp smell. A brown sublimate next formed beyond the boat. The contents of the boat were red-brown in color, melted to a dark red liquid, and gave off red-brown vapors resembling those of bromine in color. They condensed to steel-blue colored isometric forms. In every respect they indicated the tungsten hexachloride. A careful examination with a magnifying glass revealed brown needles of the pentachloride distributed around them. These could not be removed, hence the analysis made gave a result that ranges between the theoretical requirements of the penta- and hexa-

chloride. In order to weigh the product and prevent decomposition by contact with air, the tube was sealed at the contracted parts, allowed to cool, and then weighed, after which it was cracked by a hot rod, the contents dissolved out, and the tube refilled with carbon dioxide and reweighed.

0.2562 gram = material.
0.1559 gram = WO_3 obtained by ignition.
0.1236 gram = W equivalent.

48.25 = per cent. of tungsten obtained.
46.34 = per cent. of tungsten in WCl_6.
50.89 = per cent. of tungsten in WCl_5.

It may also be observed that the intensity of the heat applied, as well as its duration, had much to do with the quantity of brown material produced. This is not surprising, if the fact be recalled that the hexachloride passes into the pentachloride by ignition in carbon dioxide or hydrogen.

The analysis of another, bright red and more volatile product, showed it to be tungsten oxytetrachloride, $WOCl_4$.

0.0632 gram = material.
0.0423 gram = WO_3 obtained by ignition.
0.03352 gram = W equivalent.

53.05 = per cent. of tungsten obtained.
53.86 = theoretical per cent. of W in $WOCl_4$.

These experiments were repeated with essentially the same results so that I feel Teclu is justified in asserting that $1WO_3 + 5PCl_5$ give, as direct products, tungsten hexachloride and phosphorus oxychloride. My mode of procedure being somewhat different from that of Teclu will at once explain why in addition to phosphorus oxychloride and tungsten hexachloride, I also got the tungsten pentachloride and oxychloride.

An atmosphere of nitrogen instead of carbon dioxide was tried and gave the same result, but to a less satisfactory degree.

The same method of treatment was also applied to a mixture of equivalent quantities of molybdenum trioxide and phosphorus pentachloride. The reaction took place at lower temperature and was more rapid and energetic than in the case of tungsten trioxide. At first a very volatile white sublimate was deposited in the forward part of the tube, followed by copious brown

vapors. On driving these over gently, a black liquid residue was left in the boat. This solidified, on cooling, forming shining needle crystals which, on examination, proved to be molybdenum pentachloride. Owing to the immediate oxidation in contact with air it was not possible to remove other adhering lower chlorides from the boat, but the latter was at once put into a tube filled with carbon dioxide and thus weighed. The contents of the boat were then dissolved in water and nitric acid and the chlorine determined by titration with tenth normal silver nitrate, potassium chromate being used as an indicator.

0.8296 gram = material.
0.51475 gram = chlorine by silver nitrate.
63.25 = per cent. chlorine found.
64.83 = theoretical per cent. Cl in $MoCl_5$.

The low result is accounted for by the presence of lower chlorides which could not be separated.

II. *Action of Silicon Tetrachloride upon the Tungsten and Molybdenum Trioxides.*—Vapors of silicon tetrachloride were passed over tungsten trioxide while the latter was subjected to the heat of a combustion furnace. It was hoped that tungsten hexachloride might be formed according to the equation:

$$2WO_3 + 3SiCl_4 = 2WCl_6 + 3SiO_2.$$

The air was first expelled from the tube by a current of carbon dioxide and then the latter was passed through the small flask containing silicon tetrachloride which was subjected to the heat of a water-bath. No action took place, however, although the operation was continued for about two hours. When a small quantity of air was admitted, tungsten oxytetrachloride and tungstyl chloride were formed.

Silicon tetrachloride was likewise without action on molybdenum trioxide. Rauter (Dissertation, Tübingen, 1893), heated the trioxides together with silicon tetrachloride in sealed tubes. His products were oxychlorides, perhaps in great part due to the presence of air.

III. *Action of Various Gases upon Metallic Tungsten and Molybdenum.* (*a*) *Action of Nitric Oxide.*—As it was not known whether nitric oxide would have a reducing or oxidizing action it was passed over the metals as well as their trioxides, heat being

applied at the same time. The gas was generated by the action of nitric acid on copper and dried by passing through sulphuric acid. Tungsten trioxide was put into a porcelain boat and the latter into a piece of hard combustion tubing to which heat was applied with one or more Bunsen burners. Nitric oxide gas was passed through the tube and strong heat applied to the boat for half an hour or more. No change was produced on the tungsten trioxide. Molybdenum trioxide treated in a similar way was also unchanged.

Then finely powdered metallic tungsten was placed in the tube, all the air carefully expelled by the current of nitric oxide, and heat applied gradually. At a moderately high temperature (below red heat) action between the metal and nitric oxide began and then proceeded rapidly by means of the heat generated by the reaction, the contents of the boat becoming almost white hot. The product of the reaction was tungsten trioxide.

Metallic molybdenum was subjected to the same treatment. The reaction began only at red heat and proceeded rapidly but with less energy than in the case of tungsten. After continued strong ignition the result of the reaction was not the trioxide but the dioxide of molybdenum.

(*b*) *Action of Nitrous Oxide.*—Metallic tungsten was placed in the tube and the air carefully driven out of the latter before heat was applied. The action on the tungsten began just as the glass tube began to show signs of redness. The reaction was rapid, with evolution of light and heat, but less energetic than with nitric oxide. Tungsten trioxide was the final product.

Metallic molybdenum, treated in the same manner, required full red heat before any reaction took place. The product was again molybdenum dioxide.

(*c*) *Action of Nitrogen Peroxide.*—With tungsten, the action began at low temperature, hardly more than 300°–350°, and proceeded rapidly, but not with the evolution of as much light as with nitric oxide, probably for the reason that the reaction began at lower temperature. Tungsten trioxide was again the product.

With molybdenum the action began at incipient red heat, proceeded with more energy than in the preceding instances, and at once formed molybdenum trioxide.

Considering that nitrous oxide (N_2O) shows in its heat of formation (—17,740 Cal.) that it is an endothermic body, and that nitric oxide (NO) and nitrogen peroxide (NO_2 = —2,045 Cal.) are members of the same class, it is not surprising that the trioxides of the metals are not in any manner affected by them.

(*d*) *Action of Sulphur Dioxide.*—Tungsten began to be oxidized at moderately high temperature, but no evolution of light occurred. On continued application of high red heat, only lower tungsten oxides (blue, greenish, and brown) were formed and no trioxide was apparent. A deposit of sulphur was formed on the anterior part of the tube.

With molybdenum, action took place only at the highest temperature, no light being evolved. The oxidation proceeded slowly, and the final product was molybdenum dioxide. Sulphur was deposited on the walls of the tube.

In sulphur dioxide the oxygen is more firmly bound than in any other derivative of these two elements, and yet these metals, molybdenum and tungsten, are capable of withdrawing it.

(*e*) *Action of Methylamine.*—A current of this gas was generated by heating, in a small flask, a mixture of quicklime and methylamine hydrochloride, the gas being dried by passing over quicklime. The escaping gas was finally conducted into dilute hydrochloric acid. The metals, tungsten and molybdenum, were each heated in this gas. It was thought that a reaction might take place similar to that when metallic potassium is heated in methylamine, namely, the production of the cyanide of the metal. No change, however, took place with the metals, but the dilute hydrochloric acid into which the escaping gas was conducted became charged with hydrocyanic acid. This was undoubtedly produced by the methylamine becoming decomposed in passing through the red hot tube.

IV. *Action of Various Gases on the Tungsten and Molybdenum Trioxides.* (*a*) *Action of Ethylene.*—Tungsten trioxide heated in a stream of this gas began to be reduced at red heat, the reduction proceeding slowly. Water was condensed on the forward part of the tube, and a mirror of carbon was deposited near the boat. The fact of its being carbon was proved by afterward burning it, no residue being left. After applying heat for about

an hour, a gentle stream of ethylene being maintained, the tungsten trioxide was found to be reduced to a deep blue oxide, quite homogeneous. This oxide was put into an ammoniacal solution of silver nitrate, but after standing more than an hour no metallic silver was precipitated.

Molybdenum trioxide was treated in a similar manner; reduction took place more promptly and readily. A beautiful bronze-brown colored crystalline oxide was left. This was weighed and put into an ammoniacal solution of silver nitrate and digested for some time. The oxide went into solution and metallic silver was precipitated and afterward weighed.

0.0994 gram = weight of material.
0.1538 gram = weight of silver precipitated.
0.0686 gram = corresponding amount of molybdenum, according to the proportion:

$$2Ag : Mo :: 0.1538 : 0.0686.$$

69.02 = per cent. Mo in bronze-brown oxide.
70.58 = per cent. Mo in Mo_2O_5.

This result, although not as accurate as could be desired, indicates the brown oxide to be Mo_4O_{11}.

(*b*) *Action of Acetylene.*—In a stream of this gas tungsten trioxide was slowly reduced at red heat, a mixture of blue and brown oxides being the result, the latter underlying the former. It may be remarked that in all the reductions and oxidations noticed, the part of the substance near the bottom, or closest to the heat, was most readily acted on, and the reaction most completely carried out.

Molybdenum trioxide was reduced more readily and promptly than tungsten trioxide, and the same bronze-brown oxide was obtained as that from ethylene. Underlying this oxide there was a shining, crystalline, metallic-looking product. In its physical properties it resembled ordinary coke, being light and porous, and easily crushed. A portion of it was put into a silver nitrate solution previously rendered ammoniacal. Metallic silver was precipitated, but there remained black particles undissolved; dilute nitric acid was added and the solution warmed till the silver was dissolved; a black residue was left undissolved. This was filtered out, dried, and ignited on platinum foil; it was completely burned, no ash being left, thus indicating its composition

to be pure carbon. This being the case, it would indicate the probable formation of a *molybdenum carbide*. A quantitative analysis of this material was made as follows: a weighed quantity was put into an ammoniacal silver nitrate solution and gently warmed till metallic silver had separated out. It was then filtered through a weighed filter and dried at 100°–110°. After weighing, the precipitate was separated, as far as possible, from the filter, and treated with moderately dilute nitric acid and warmed. The silver was dissolved, leaving a black residue of carbon. This was brought upon a dried filter and weighed. Results as follows:

0.1312 gram = weight of "carbide."
0.9059 gram = weight of silver and carbon.
0.0083 gram = weight of carbon.
0.8976 gram = weight of silver by difference.

Calculating the equivalent amount of molybdenum

6 Ag : Mo : : 0.8976 : x
x = 0.1329 gram molybdenum.

This gives more molybdenum than the original weight of material, but disregarding this and taking the weights of molybdenum and carbon as found, and dividing by their atomic weights it gives 0.001384 molybdenum to 0.000691 carbon, or two parts molybdenum to one part carbon.

This would indicate a formula, Mo_2C.

Two other analyses were made, only the carbon being determined as above, the molybdenum being taken by difference. Results of second analysis are as follows:

0.0642 gram = weight of "carbide."
0.0026 gram = weight of carbon.

0.0616 gram = weight of molybdenum.

These results indicate the formula, Mo_3C.

The third analysis was as follows:

0.1255 gram = weight of "carbide."
0.0081 gram = weight of carbon.

0.1174 gram = weight of molybdenum.

This approximates the formula, Mo_2C, as found in the first analysis. It may be that it is not a definite chemical compound but only a mixture, though the yields obtained at different times

for the foregoing analyses had all the same appearance and physical properties. A further investigation of this compound will be made.

(*c*) *Action of Methane.*—Tungsten trioxide was heated in methane at the highest heat of a Bunsen burner for nearly an hour with no apparent reduction. The full heat of a blast-lamp was then applied which caused the reduction of tungsten trioxide to the blue oxide, W_2O_5.

Molybdenum trioxide began to be reduced at the ordinary heat of a Bunsen flame. After heating thus to redness for about half an hour the boat was found to contain both metallic molybdenum and the dioxide, the former being underneath the latter.

(*d*) *Action of Ethane.*—Neither of the trioxides was affected by this gas, though heated for upwards of half an hour.

(*e*) *Action of Phosphine.*—Tungsten trioxide was first placed in the tube. Reduction began when the flame had been played under the boat only a few times, so that the temperature could not have been above 125°–150°. Even before any reducing effect was noticed, a faint white vapor rose from the boat but soon disappeared. The reaction proceeded rapidly, leaving a deep-blue colored product in the boat. A sublimate of phosphorus was formed on the sides of the tube. A portion of the blue oxide was weighed off and ignited to the trioxide in order to determine the percentage of tungsten.

0.0563 gram = weight of material.
0.05645 gram = WO_3 obtained by ignition.
0.04477 gram = corresponding weight of W.
79.52 = per cent. tungsten.

This result seems to correspond to the theoretical 79.70 per cent. of tungsten in the oxide W_2O_5. In another portion of the blue oxide, phosphorus was determined by digesting with nitric acid, thus converting any phosphorus into phosphoric acid, neutralizing with ammonia, and precipitating with "magnesia mixture." The amount of phosphorus found was only between one and two per cent., indicating that it was probably only mechanically admixed with the oxide. A further confirmation of this is the fact that the sides and edges of the boat were observed to be moist after brief standing in air.

Molybdenum trioxide began to show signs of reduction without any application of heat, and when heat was applied in the gentlest way the reduction proceeded rapidly. As in the case of tungsten a faint white vapor was first formed. There was left a beautiful, lustrous, crystalline product with royal-purple color. A yellow film of phosphorus was formed on the sides of the tube. A portion of the purple oxide was ignited to trioxide with the following result:

0.0452 gram = weight of material.
0.0476 gram = MoO_3 obtained by ignition.
0.03173 gram = corresponding weight of Mo.
70.20 = per cent. molybdenum.

This corresponds to the theoretical 70.58 per cent. molybdenum in the oxide Mo_2O_5.

Another portion, treated with nitric acid, was completely dissolved; only 1.99 per cent. of phosphorus was found, hence it could not have been chemically combined, but came from phosphorus that had been deposited on the boat.

Ammonia acts upon both tungsten and molybdenum trioxides more energetically, and the products of the reaction are far more complicated than in the above instances. The less basic character of phosphine compared with ammonia explains the difference.

(*f*) *Action of Arsine.*—The products were the same blue and purple oxides that were obtained with phosphine, but the reduction took place much more sluggishly. As usual, molybdenum trioxide was the more readily reduced. Much metallic arsenic was formed on the sides of the tube. Only a comparatively gentle heat was applied, owing to the ready decomposability of arsine.

A commonly occurring statement made in regard to the hydrides of nitrogen, phosphorus, and arsenic, is that basicity diminishes with rise of atomic mass; hence it is not surprising that arsine should show the sluggish behavior noted above.

V. *Reduction of the Tungsten and Molybdenum Trioxides by Magnesium, Zinc, and Aluminum.*—(*a*) *Action of Magnesium.*—Tungsten trioxide and powdered magnesium in molecular proportions were mixed and heated in a small glass tube drawn out

to a point. At a low temperature the magnesium was oxidized with a little puff, light being evolved. A gray to black residue was left. This was digested with dilute hydrochloric acid which left a black or slightly grayish residue. A portion of this was weighed off and ignited to tungsten trioxide in order to determine the percentage of tungsten.

0.0858 gram = weight of material.
0.0928 gram = WO_3 obtained by ignition.
0.0736 gram = W corresponding.
85.76 = per cent. tungsten.

This corresponds to the theoretical 85.18 per cent. tungsten in tungsten dioxide, thus showing that the trioxide is reduced to dioxide by magnesium.

The reduction of molybdenum trioxide took place in a similar manner, a black residue being left. This was digested with dilute hydrochloric acid and the molybdenum determined by ignition to the trioxide.

0.0386 gram = weight of material.
0.0466 gram = MoO_3 obtained by ignition.
0.03106 gram = Mo corresponding.
80.48 = per cent. Mo.

This corresponds to the theoretical 80.00 per cent. molybdenum in the sesquioxide, and seems to indicate that magnesium reduces molybdenum trioxide to sesquioxide.

These reductions were also carried out in an atmosphere of hydrogen. At a comparatively low temperature, hardly above 350°, the action between magnesium and tungsten trioxide took place with a little flash of light and the evolution of sufficient heat to crack the combustion tube in which the operation was being performed. The residue was dark gray to black, and looked somewhat metallic. The percentage of tungsten was determined as before.

0.10085 gram = weight of material.
0.1114 gram = WO_3 obtained by ignition.
0.08835 gram = W corresponding.
87.60 = per cent. tungsten.

This seems to indicate the formation of the sesquioxide which contains 88.46 per cent. of tungsten.

Molybdenum trioxide was reduced at even lower temperature,

with formation of the dioxide as shown by the following analysis:

0.1050 gram = weight of material.
0.1214 gram = MoO_3 obtained by ignition.
0.08093 gram = Mo corresponding.
77.07 = per cent. Mo.
75.00 = per cent. Mo in MoO_2.

The trioxide obtained by ignition was apparently not homogeneous; this fact taken together with the above variation from the theoretical per cent. makes the above result more than doubtful. Besides, it is hardly likely that a lower oxide would be obtained by reduction in air than in hydrogen.

(*b*) *Action of Zinc.*—The experiments with metallic zinc were carried out in the same manner as those with magnesium. Heated in air, in a drawn out tube, the mixture of tungsten trioxide and zinc dust began to react at a moderate heat (300°–400°), the reduction proceeding slowly throughout the mass without the evolution of light. The residue was a gray to brown mixture, which the estimation of tungsten indicated to be the oxide W_2O_5.

0.1169 gram = weight of material.
0.12064 gram = WO_3 obtained by ignition.
0.09568 gram = W corresponding.
81.84 = per cent. tungsten.
82.12 = per cent. W in W_2O_5.

Molybdenum trioxide mixed with zinc dust and heated was reduced more readily and at lower temperature than tungsten trioxide. The action was also more energetic, being concluded with a little explosive puff. Examination of the residue indicated it to be probably Mo_2O_5.

0.1028 gram = weight of material.
0.1109 gram = MoO_3 obtained by ignition.
0.07393 gram = Mo corresponding.
71.91 = per cent. Mo.
70.58 = per cent. Mo in Mo_2O_5.

These two experiments with zinc were then repeated in a current of hydrogen. Tungsten trioxide was easily and gradually reduced at about the same temperature as before. The product was brownish; analysis showed it to be the dioxide.

0.11295 gram = weight of material.
0.1202 gram = WO_3 obtained by ignition.
0.09533 gram = W corresponding.
84.40 = per cent. tungsten.
85.18 = per cent. W in WO_2.

Molybdenum trioxide was easily reduced at low temperature, the reaction taking place with a slight puff. The product was brownish in color. Analysis as follows:

0.1070 gram = weight of material.
0.1164 gram = MoO_3 obtained by ignition.
0.0776 gram = Mo corresponding.
72.52 = per cent. Mo obtained.
70.58 = per cent. Mo in Mo_2O_5; 75.00 = per cent. Mo in MoO_2.

Thus the product seems to be an intermediate one, but this was doubtless caused by impurities. The brownish color of the product suggests, perhaps, that it is the dioxide. If there were an oxide with the composition Mo_4O_9, it would have 72.72 per cent. of molybdenum, which is quite close to the percentage actually obtained.

(*c*) *Action of Aluminum.*—The trioxides were intimately mixed with molecular quantities of powdered aluminum, placed in a glass tube three or four inches long, sealed at one end, and heated.

With tungsten trioxide there was no action till full red heat was reached when there was a flash and slight report, cracking the tube and scattering its contents. There was not enough material left for analysis, but the walls of the tube were coated with a brownish oxide, probably the dioxide.

With molybdenum trioxide the action was similar, but took place at somewhat lower temperature and was not quite so violent. The sides of the tube were covered with dark blue oxide, probably Mo_2O_5.

These experiments were repeated in an atmosphere of hydrogen but were not successful as no reaction took place. This is undoubtedly for the reason that the temperature required is so high that the trioxides were reduced by the hydrogen before action with aluminum could take place.

At least one interesting fact is brought out by these experiments on oxidation and reduction, and that is that there is a

considerably stronger affinity between tungsten and oxygen than there is between molybdenum and oxygen. This is proved by the fact that in every case the former metal was more readily oxidized while its trioxide was reduced with more difficulty. This is also further illustrated by the experiments with ferric chloride next to be described.

VI. *Reduction of Ferric Chloride by the Metals, Tungsten and Molybdenum.*—A solution of ferric chloride of known strength was made by dissolving piano wire in hydrochloric acid, oxidizing with nitric acid, and evaporating on the water-bath with addition of hydrochloric acid. It was then taken up with water, a few drops of hydrochloric acid added to dissolve basic salts, and the solution, containing 1.11293 grams iron, diluted to one liter.

First a general experiment was made by putting a small indefinite quantity of each metal, in a finely divided state, into an indefinite quantity of ferric chloride solution and a few drops of hydrochloric acid added. The solution containing molybdenum, after standing an hour or so with frequent stirring, lost the yellow color of the ferric salt, hence more was added. The liquid was then largely diluted, a little sulphuric acid added, and a titration made with potassium permanganate to ascertain if reduction of the ferric salt had taken place. A very considerable quantity of ferrous salt was found to be present. The solution containing tungsten stood for several hours but no discharge of color of the ferric salt was noticed. Titration with permanganate however showed a small amount of ferrous salt to be present.

Quantitative experiments were then made to ascertain the relation between the amounts of molybdenum and tungsten and the quantity of ferrous chloride produced. Very small quantities of the metals were taken, as the qualitative experiments showed that the amounts taken for those tests would require a very large amount of ferric solution.

(*a*) *Molybdenum.*

First Experiment:

0.0040 gram = weight of molybdenum taken.
0.01321 gram = metallic iron found by titration.
0.01382 gram = metallic iron equivalent to 0.0040 gram Mo.

according to the proportion:

Mo : 6Fe : : 0.0040 : 0.01382.
Error = 0.00061 gram.

Twenty-five cc. of the ferric solution were used containing 0.02782 gram metallic iron. The molybdenum was completely dissolved. Time of experiment one to two hours. The experiment shows also that 1 Mo is equivalent to 6Fe according to the equation,

$$6FeCl_3 + Mo = MoCl_6 + 6FeCl_2.$$

Second Experiment:

0.00445 gram = molybdenum taken.
0.01566 gram = iron found by titration.
0.01557 gram = iron equivalent to 0.00445 gram Mo.
Error = 0.00009 gram.

All the molybdenum was completely dissolved.

Time, one to two hours.

Twenty-five cc. of ferric solution used.

Third Experiment:

0.0867 gram = molybdenum taken.

The action with this larger quantity of metal was very slow, and after standing for about forty hours there was still a considerable amount of metal not dissolved.

Fourth Experiment:

In this experiment a more concentrated solution of ferric chloride was used containing 11.4022 grams metallic iron to one liter.

0.07857 gram = molybdenum taken.
0.26702 gram = iron found by titration.
0.27499 gram = iron equivalent to 0.07857 gram Mo.
Error = 0.00797.

That is, only 97.10 per cent. of the molybdenum had gone into solution. This solution stood forty-eight hours and there were still small solid particles to be noticed suspended in the solution.

It seems from the foregoing experiments that complete solution and reduction do not take place in a reasonable length of time, except with small quantities of the metal. The results of the first two experiments are interesting as throwing further

light on the valency of molybdenum, and in suggesting an excellent method for the accurate determination of the atomic mass of this metal as compared with iron.

(*b*) *Tungsten.*

First Experiment:

0.0042 gram = tungsten taken.
0.0007345 gram = iron found by titration.
0.00767 gram = iron equivalent to 0.0042 gram tungsten.

according to the proportion:

W : 6Fe :: 0.0042 : 0.00767
9.57 = per cent. of tungsten dissolved.

Time, two hours.

Second Experiment:

0.00446 gram = tungsten taken.
0.001958 gram = iron found by titration.
0.00814 gram = iron equivalent to 0.00446 gram tungsten.
24.05 = per cent. of tungsten dissolved.

Time, four hours.

Third Experiment:

0.00516 gram = tungsten taken.
0.002692 gram = iron found by titration.
0.009422 gram = iron equivalent to 0.00516 gram tungsten.
28.57 = per cent. of tungsten dissolved.

Time, six hours.

Fourth Experiment:

0.00475 gram = tungsten taken.
0.005237 gram = iron found by titration.
0.00863 gram = iron equivalent to 0.00475 gram tungsten.
60.69 = per cent. of tungsten dissolved.

Time, eight hours.

These experiments were made with the more concentrated ferric chloride solution. There is seen to be a gradual increase in the amount of iron reduced, roughly proportional to the time; but complete solution of tungsten could not be obtained, although small portions were allowed to remain over forty-eight hours in the ferric solution.

This reducing power of molybdenum and tungsten, indicated in the preceding experiments, is further corroboration of the

experiments made by Smith (*Ztschr. anorg. Chem.*, **1**, 360), with these metals and solutions of silver, gold, and mercury salts. It is further additional comparative evidence of the conduct of the metals of this subdivision of group VI. Of the behavior of chromium in this direction we have no experimental evidence, but of uranium it is known that it reduces salts of tin, platinum, gold, copper, mercury, and silver to the metallic condition. With molybdenum the reduction with these metals proceeds quite rapidly, but the speed diminishes with rise in atomic mass, so that the sluggish action of tungsten in ferric salts is not surprising.

THE DETERMINATION OF SULPHUR IN PYRITES.

A REPLY TO DR. LUNGE.

By Thomas S. Gladding.

Received March 5, 1895.

IN this JOURNAL (June *1894*) I published an investigation of the several methods of estimating sulphur in pyrites. As a result of that investigation I rejected all other methods and recommended, in the strongest terms, the general scheme published by Dr. Lunge in his "Alkali-makers' Handbook." At the same time I advised a few minor modifications as conducive to greater certainty and accuracy. In this JOURNAL (March *1895*) Dr. Lunge makes a vigorous attack upon each and every one of these modifications. An examination of his paper brings out the important fact that he admits that every modification proposed is accurate in its nature with one single exception. Unfortunately for Dr. Lunge, the single feature selected for condemnation is the one most easily capable of rigid and positive proof as to its absolute accuracy. I shall reserve the consideration of this point and take up in order the modifications to which such strenuous objection is made.

He objects to the use of one gram instead of half a gram. In reply I have found that by my method one gram is as easily handled as one-half gram and double the accuracy is attained in consequence. He objects to the use of a bromine solution instead of aqua regia as a solvent for pyrites. This substitution was made for the reason that quite often when using aqua regia I was annoyed by the separation of free sulphur. Since adopt-

ing the bromine solution I have *never* experienced this trouble.

His first important objection is against my direction to *always* dissolve the ferric hydroxide and test the same for sulphur. He declares that such procedure is unnecessary. On reading his comments on this point, however, we find that he admits that students in his own laboratory have sometimes failed to get out all the sulphur, through imperfect washing. He further "grants that in important cases the ferric hydroxide ought to be tested in some way or another for any sulphur left behind." If the washing out of *all* the sulphur is so absolutely certain as he claims elsewhere, why, it may be asked, does he grant what he does? The concession which he makes is a confession of uneasiness of mind on this very point and is all that I could ask for to justify my own instructions. In answer to his criticisms I will simply state that my washing of the precipitated hydroxide was made exactly as he directs. Five or six washings with hot water, "thoroughly churning" up the precipitate each time has never yet, in my hands nor in those of our assistants, completely removed all the sulphur when using one gram. When using one-half gram the danger of losing sulphur would undoubtedly be much lessened, but no careful analyst will neglect the very simple precaution of dissolving the ferric hydroxide in dilute hydrochloric acid and adding ten cc. of barium chloride to the filtrate.

Lunge's second objection is to my addition of the barium chloride solution, one drop per second, to the boiling sulphate solution. He admits that this method is entirely accurate but tedious and unnecessary, taking "about an hour." In reply I will first state that such addition requires only fifteen minutes, and as it is done automatically from a burette, requires no more labor than it does to "pour it in all at once."

But still further I condemn, as inaccurate, Lunge's method of adding the barium chloride all at once. The following comparative tests made, in part, by our assistant Mr. H. E. Cutts and, in part, by myself personally, are very conclusive on this point. A number of samples of pyrites were treated exactly alike in every respect except in the method of adding the barium chloride.

By slow addition. Per cent.	By sudden addition. Per cent.
50.23	50.84
51.00	51.20
51.00	51.32
51.20	51.50
39.13	39.35
39.40	39.90

In the last three samples the filtrates from the ferric hydroxide were divided into two equal portions, and one portion treated in the first manner, the other in the second. Still further tests were made by dissolving two and seven-tenths grams of chemically pure potassium sulphate in 400 cc. of water, adding five cc. of hydrochloric acid and treating as above.

By slow addition.		By sudden addition.
0.4960		0.4990
0.4960	Theory 0.4965	0.5020
		0.5021

I have also taken two grams of chemically pure ammonium sulphate, thus imitating more exactly the conditions of the pyrites analysis as carried out by Lunge and obtained

By slow addition.	By sudden addition.
0.4838 gram sulphur	0.4858
0.4828 " "	0.4900
0.4834 " "	0.4888

Theory calls for 0.4848. The sudden addition of the barium chloride invariably gives results too high.

I quote the following private communication from Prof. Richards, of Harvard College, on this point. "I am much surprised to find that Lunge is ignorant of the occlusion of barium chloride by barium sulphate. This has been known for a number of decades. In 1890 it was so well known to me that I treated it as a matter of course (Amer. Acad. Proc., **26,** 258). This year one of my students has finished a comprehensive work upon this subject showing the amount and circumstances of the occlusion. The paper has already gone to press in the Proceedings of the American Academy and the *Ztschr. anorg. Chem.* It wholly confirms your unpublished statements made to Lunge." This is strong testimony corroborating my results given above. My method of avoiding the occlusion of barium chloride by adding the barium chloride solution *drop by drop* and thus insuring the formation of a chemically pure granular precipitate of barium sul-

phate is the same as that adopted by our National Association of Agricultural Chemists in the precipitation of phosphoric acid as ammonium magnesium phosphate.

The last objection of Lunge refers to my method of estimating the 0.20 to 0.40 per cent. of sulphur that may be left in the ferric hydroxide, by the simple plan of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium chloride solution and letting stand over night. This he declares is decidedly *wrong*.

Here again I will quote from Prof. Richards' letter. "This last paper (Dr. Lunge's) seems to me to contain several errors. I think you will find that *in the presence of a considerable excess of barium chloride*, barium sulphate is *not* very seriously soluble in cold ferric chloride solutions, even when acid (see Jannasch and Richards, *J. prakt. Chem.*, **39**, 328-329). Hence your method is as accurate as most analytical methods.

I wish to call especial attention to the method that Lunge has adopted to support his position on this point. He has taken four samples of pyrites and carried them through a complete analysis by his scheme and also by mine and because his method gives 0.20 per cent. more than mine he concludes that I lose 0.20 per cent. sulphur by the solubility of the barium sulphate in the acid solution of the ferric hydroxide. No such conclusion can be fairly drawn from so unscientific a procedure. A far better plan is to divest the problem of all other possibly interfering errors and strip it down to the naked question in hand. This had been done in my first paper as follows:

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1. Sulphur..... 0.0049 gram.
2. " ..... 0.0050 "
3. " ..... 0.0051 "

The amount actually present was 0.00496 gram.

I have since repeated the above demonstration by an even more rigid test as follows: I dissolved 0.0135 gram of potassium sulphate in 100 cc. of water, added ten cc. of concentrated

hydrochloric acid, one-half gram of iron, ten cc. of barium chloride solution, precipitating hot and allowing to stand as above. The barium sulphate came down slowly, on cooling. The ignited barium sulphate was snow-white and free from iron, probably on account of its slow formation; I obtained:

1. Sulphur..... 0.0025
2. " 0.0026

The amount actually present was 0.00248.

This amount taken in these last experiments corresponds to about 0.20 per cent. sulphur calculated on one gram of pyrites. Lunge claims to have lost this amount on account of the solubility of barium sulphate in acid solution. Were he correct I should have had no precipitate whatever in my experiments above. On the contrary I obtained the whole of the sulphur present to the one-hundredth of a per cent.

To determine sulphur in iron, Troilius, page 38, directs to "dissolve five grams in aqua regia, evaporate to dryness to make silica insoluble. To the filtrate from the silica, which should amount to at least 300 cc., a few cubic centimeters of barium chloride solution are added. After standing one night at the temperature of the room the barium sulphate is completely precipitated." Here we have ten times the amount of iron present that is contained in one gram of pyrites and yet no sulphur is lost. Had Lunge followed the safer and more scientific plan of testing this and also each of the other points in dispute, in the same way that I adopted in my original paper, namely, by working with known amounts of chemically pure salts containing known amounts of sulphur, he would not have fallen into the errors he has.

In conclusion: Of the main modifications proposed by me, Dr. Lunge admits that all are entirely correct, with one exception. The one which he claims to be inaccurate I have incontestably proven to be wholly right. I have also shown that the modification of adding barium chloride, drop by drop, is absolutely necessary to accurate results. I have also shown that the solution of the ferric hydroxide and testing the same for sulphur is certainly the safer course. I conscientiously advise my brother chemists to modify Lunge's method in accordance with my instructions.

ACIDITY OF GLUCOSE SYRUP AND GRAPE-SUGAR.

By Horace E. Horton.

Received February 18, 1895.

AN examination of glucose syrups and grape-sugars will show an acid reaction, and this acidity is due to acid calcium phosphate (rarely), hydrochloric acid, sulphuric acid, and in most instances to sulphurous acid.

The thin liquor obtained by the inversion of starch by acids is strongly acid, and this acidity is reduced by the use of calcium or sodium carbonate to 0.015 gram of hydrochloric acid in 100 grams of liquor.

Acidity due to calcium superphosphate comes from "souring" the bone-black with too strong muriatic acid, when the tricalcium phosphate is broken up with the formation of superphosphate; when a special phosphate black is used in the manufacture of goods, from the occluded superphosphate. I am convinced that in one instance at least, free phosphoric acid had been added to the sample to secure good color.

Sulphurous acid is added to the glucose syrup or grape-sugar when in the cooler.

The acidity is expressed in grams hydrochloric acid or sulphur dioxide in 100 grams substance.

The determination of the acidity was made as follows: 100 grams of glucose or grape-sugar weighed into a beaker and dissolved in about 200 cc. of hot water. A small quantity of carefully prepared delicate litmus solution added, and then titrated with $\frac{N}{10}$ potassium hydroxide.

I have determined the acidity of a number of American brands with the following results:

Chas. Pope Glucose Co.

Geneva XXX. 0.0080 sulphur dioxide.
" Jelly 43° Bé. 0.0136 " "

Chicago Sugar Refining Co.

Confectioners Glucose, 0.012 0.018 0.018 0.018 0.018 0.015 SO_2.

AMERICAN GLUCOSE CO.

41° Bé. Mixing Glucose,		0.0184	0.016	0.019	0.014		SO_2.
42° " Crystal Glucose,		0.0184	0.0165	0.0205	0.0205		".
43° " Confectioners' Glucose,		0.0184	0.0184	0.0190	0.0184	0.020	"
42° " Brewers' Jelly,		0.0164	0.0164	0.0142	0.0123		"
44° " Export,		0.0172	0.021	0.023			"
42° " Acid Glucose,		0.050	0.048	0.052	0.064	0.0505	"
45° " Export,		0.0225	0.0201				"
"70" Sugar,	0.036	0.032	0.0279	0.021	0.019		HCl.
	0.016	0.018	0.017	0.027	0.028		"
	0.0295	0.0286	0.032	0.040	0.040		"
	0.045	0.0408	0.043				"

WAVERLY FARM, TOPEKA, KAN.,
February 14, 1895.

ASH IN GLUCOSE SYRUP AND GRAPE-SUGAR.

BY H. E. HORTON.

Received February 18, 1895.

OF the quantity of ash in glucose syrup and grape-sugar now offered in open market, little is published. Wishing to throw some light on this subject I present figures obtained on analysis of a number of American brands.

The ash determinations were made as follows: Five to ten grams of syrup or sugar weighed in a platinum dish of about 100 cc. capacity, heated with great care until water is expelled, slowly carbonized, and then heated in a muffle at low redness to a finish.

Hydrated grape-sugar, so-called "70" sugar, manufactured by the American Glucose Co.:

Per cent.							
0.536	0.540	0.510	0.510	0.530	0.67	0.31	0.22
0.536	0.540						

Samples of "Special Coloring," American Glucose Co.:

Per cent.		Per cent.
0.31	to	0.52

Samples of "Climax" or "Acme" sugars, manufactured by American Glucose Co.:

"Special dark."	"Dark."	"Light."
0.205	0.16	0.15

"Brewers' sugar," manufactured by Chicago Sugar Refining Co.:

"White."	"Standard."	"Special dark."
Per cent.	Per cent.	Per cent.
0.74	1.00	0.51
0.73	0.72	0.74
	1.15	0.43

"Brewers extract," Chicago Sugar Refining Co., 0.46 per cent.

American Glucose Co., glucose syrups:

	Per cent.		
43° Bé. confectioners' glucose,	0.81	0.33	0.74
41° " mixing glucose,	0.24	0.24	0.26

Chicago Sugar Refining Co.:

	Per cent.		
41° Bé. glucose,	0.14	0.12	0.13
43° " "	1.10	0.65	

National Starch Manufacturing Co., Glen Cove Factory., confectioners' glucose:

Per cent.		
0.80	0.77	0.46

Chas. Pope Glucose., confectioners' glucose, 0.84 per cent.

Peoria Grape-Sugar Works:

41° Bé. glucose,	0.26	0.28	0.26

The composition of the ash varies with the process of manufacture. If the starch be inverted with muriatic acid and neutralized with sodium carbonate and hydroxide, the ash in finished product will sometimes run over one per cent. and consist almost entirely of sodium chloride.

When oxalic acid is used for inverting and calcium carbonate for neutralizing, calcium oxalate, which is sparingly soluble in glucose solutions, will be found present in glucose, and go over into carbonate on ashing.

When calcium sulphate is used for "brightening" the glucose, a large quantity of it will be present in the ash.

The ash of oxalic acid glucose will contain a small amount of chlorides, coming from muriatic acid used for "souring" the bone, from muriatic added with bisulphite to finished goods in cooler, from sodium chloride by decomposition of calcium chlo-

ride with sodium sulphate after neutralizing, and also from the calcium chloride when the liquor does not receive sufficient sodium sulphate for complete decomposition.

When special prepared phosphate bone is used in the manufacture of syrup and sugar, phosphates are found in the ash. I have found as high as nineteen per cent. of phosphorus pentoxide present.

Iron is present in every ash. It is introduced into the process at the outset and is taken out and as often replaced up to the finish. Batches of glucose made from thin liquor first boiled in a vacuum pan after boiling out with muriatic acid, contain an abnormal amount of iron.

WAVERLY FARM, TOPEKA, KAN.,
January 20, 1895.

THE ZIMMERMANN-REINHARDT METHOD FOR THE DETERMINATION OF IRON IN IRON ORES.[1]

BY C. T. MIXER AND H. W. DUBOIS.

Received March 6, 1895.

THE methods chiefly employed in this country for the determination of iron in ores, are the permanganate and Kessler's modification of the old bichromate method (Penny's).

Recently a method has been proposed by R. W. Mahon in the *American Chemical Journal*, **15**, 360. The chief feature of this method consists in the proposed use of an indicator solution, for titration with stannous chloride. The indicator solution consists of platinic and mercuric chlorides, the end reaction being indicated by the darkening of the mercurous chloride (formed by the slight excess of stannous chloride), which is caused by the formation of mercurous platinochloride.

As regards this method, it would seem that the frequent standardizations of the stannous chloride that must be made, is a serious objection, and further, the indicator which is used, cannot compare in distinctness with that produced by potassium permanganate.

The objections to the first two methods are mainly those of time consumed in their operation, which specially concerns those who have to make large numbers of determinations. Their general accuracy can hardly be questioned.

[1] This article includes the modifications of the method, as practiced in the Lake Superior iron region.

A preliminary note of the method to be described, appeared in the *Engineering and Mining Journal*, April 14, *1894*.

It has been used with most excellent results during the past few years in some of the laboratories on the Lake Superior iron ranges.

The standard works on chemical analysis contain no reference to this method. Furman in his Manual of Practical Assaying, page 173, refers rather indifferently to the use of manganous sulphate for titrating in a hydrochloric acid solution with potassium permanganate, but does not seem to be aware of the rapid and accurate method which can be formulated by its use.

Methods have been proposed for titrating directly in a hydrochloric acid solution, but have never proved to be practicable for technical analysis.[1]

The chlorine liberated under such circumstances, seriously affects the results, and it is by the use of manganous sulphate that this is prevented. The use of the above salt for this purpose was first proposed by C. Zimmermann.[2] In this article there is simply outlined the efficacy of manganous sulphate for titrating in hydrochloric acid solutions. Zinc was employed for reduction. A large number of analyses are given, showing the agreement between results obtained from sulphuric acid solutions and hydrochloric acid solutions treated in this manner.

Reinhardt[3] suggested the improvements of reducing with stannous chloride and taking up the excess of the latter, with mercuric chloride, which was then, as now, used in connection with the bichromate method. Later[4] he gives a comprehensive review of the method and suggests a very valuable improvement in the addition of sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid allows the formation of iron phosphate, which being nearly colorless, renders the end reaction more distinct. Otherwise, the presence of the yellow iron chloride will greatly obscure the end reaction.

The solutions required are as follows:

[1] Löwenthal and Lenssen, *Ztschr. anal. Chem.*, 1, 329, and David H. Browne, *J. Anal. Appl. Chem.*, 5, 362.

[2] *Ber. d. chem. Ges.*, *1884* Jahrgang, 15, 779.

[3] Stahl und Eisen, Jahrgang, 4, 704.

[4] *Chem. Ztg.*, Jahrgang, 13, 323. The Journal of the Iron and Steel Institute, *1889*, 1, 400, gives a synopsis of this article and an incorrect reference to it.

Solution A. Stannous Chloride.—One pound of stannous chloride is dissolved in one pound of hydrochloric acid 1.2 sp. gr., to which water has been added and, when dissolved, is diluted to two liters.

Solution B. Hydrochloric Acid 1.1 sp. gr.—Made by mixing equal volumes of acid 1.2 sp. gr. and water.

Solution C. Mercuric Chloride.—A saturated solution is made by dissolving in hot water, allowing to cool and crystallize, and then filtering.

Solution D.—One hundred and sixty grams of manganous sulphate are dissolved in water and diluted to 1750 cc. with water. To this are added 330 cc.[1] of phosphoric acid (syrup), 1.7 sp. gr., and 320 cc. of sulphuric acid, sp. gr. 1.84.

This solution permits the titration to be made in a hydrochloric acid solution and thus obviates the deleterious action of the chlorine that is liberated by the action of the hydrochloric acid on the potassium permanganate.

Solution E. Potassium Permanganate.—Two hundred and fifty grams of potassium permanganate are dissolved in water and diluted to fill an ordinary carboy (about 44 liters). For more accurate determinations, a solution just one-half this strength is used. For the weight we employ, the main solution has the strength, such that one cc. equals two per cent. This solution is standardized by means of an iron ore, the exact value of which has been ascertained in a number of different ways.

The Standardization.—For ordinary commercial work, less than one-half gram of the standard ore is taken, the precise weight being so adjusted that one cc. of the potassium permanganate solution is equivalent to two per cent. of iron. Thus, if the standard ore contain 61.20 per cent. of iron, the weight would be so taken, that the reading of the burette would be 30.6 cc. If, however, it should be 30.7 cc., then either the weight would be diminished in the proportion of 30.6 : 30.7, or one-tenth cc. would be subtracted on all subsequent readings of the burette. The latter is the method generally employed when the discrepancy is so slight as this. For the obtaining of the percentage,

[1] Reinhardt recommends a solution more than twice this strength of phosphoric acid, but we have found the above quantity sufficient.

the burette reading is doubled, after making the correction, if such be necessary.

It will be found conducive to accuracy, and require very little extra work, to accompany each series of determinations by a standard ore, which, being under precisely the same conditions, any error in weight or solutions will immediately be detected.

The Method.—About one-half gram of ore (exact weight depending, as shown above, upon the standard ore) is placed in a No. o lipless beaker, and two and five-tenths cc. of stannous chloride (*Solution A*) added, this being a sufficient amount for ores analyzing between fifty-five and sixty-five per cent. of iron. It is advisable to use a little less for leaner ores. Then ten to fifteen cc. of hydrochloric acid is added (*Solution B*), and, placing a watch-glass on the beaker, the contents are allowed to boil gently on an iron plate until the ore is completely dissolved.

This will generally require only a few minutes, depending mainly on the character of the ore.

When the ore is dissolved, and while the solution is still hot, additional drops of stannous chloride are added from a burette, until all the iron is just reduced to the ferrous state, which is indicated by the disappearance of the greenish-yellow color.

In case a number of ores are being analyzed, it will be found more convenient to bring several of the solutions up to this point and then slightly oxidize them by the addition of a few drops of the potassium permanganate solution.

In case an excess of stannous chloride has been added originally, the solution is also oxidized as above.

The solution, in its slightly oxidized condition, should be kept warm, and the final reduction be made by a drop or two of stannous chloride. It is desirable to have the least possible excess of stannous chloride, after complete reduction has taken place.

During this operation of reduction and oxidation, the solution is constantly agitated by giving the beaker a rotating motion, which alternates in opposite directions.

The final reduction having been made, the sides of the beaker are washed down and five cc. of mercuric chloride (*Solution C*)

added to take up the excess of stannous chloride, which forms a white silky precipitate of mercurous chloride.

After the addition of mercuric chloride, the contents of the beaker are washed immediately into a 500 cc. beaker, in which has been placed six to eight cc. of *Solution D* and about 400 cc. of water. The solution is now ready for titration.

Ores containing organic matter, some magnetites, and pyritous ores, require the usual precautions. With ores containing very large amounts of organic matter, it is generally most advantageous to burn off directly and follow with the regular method. Ores containing small amounts of organic matter, and pyritous ores, are dissolved in hydrochloric acid and oxidized with potassium chlorate, after which the regular method is pursued.

The use of stannous chloride to hasten the solution of an ore, is particularly convenient in laboratories located in the mining regions. Reinhardt does not mention the use of it. We are not able to state who first proposed its use, but it is not improbable that it may have been accidentally devised independently, by several chemists.

The action of the stannous chloride is doubtless that of converting the iron sesquioxide into the more basic protoxide, towards which the hydrochloric acid asserts a more powerful solvent action.

A tabulation of some results is here given showing the relative rates of dissolving with hydrochloric acid alone, and hydrochloric acid and stannous chloride.

Ore.	No.	Solvent.	Time required for solution.	Iron in Residue.
Soft hematite,	1A	$HCl + SnCl_2$	2 min.	0.11
	B	HCl	26 "	0.22
Soft hematite,	2A	$HCl + SnCl_2$	4 "	0.09
	B	HCl	35 "	0.12
Specular hematite,	3A	$HCl + SnCl_2$	6 "	0.09
	B	HCl	24 "	0.10
Blue granular ore,	4A	$HCl + SnCl_2$	6 "	0.18
(Hematite)	B	HCl	30 "	0.21

In order to compare the results afforded by this method with other methods, the following tabulation of analyses has been prepared.

No.	Chemist.	Location.	Ore.	Method.	Per-cent.	Mixer and DuBois Zimmermann-Reinhardt Method.
1	B. E. LaLonde,	Pittsburg and Lake Angeline Iron Co.	Lake Angeline Hematite.	Bichromate.	63.40	63.40
2	A. G. McKenna,	Edgar Thompson Steel Works.	Pewabic.	"	64.75	64.80
3	A. G. McKenna,	Edgar Thompson Steel Works.	Toledo.	"	41.30	41.20
4	E. P. Jennings,	Ironwood, Mich.		"	61.95	62.05
5	E. E. Brewster,	Iron Mountain, Mich.	Pewabic.	"	63.32	63.38
6	Lerch Bros.	Virginia, Minn.	Mesabi.	Permanganate.	67.44	67.26
7	Porter W. Shimer,	Easton, Pa.	Alabama "fossil ore."	"	48.36	48.25
8	W. E. Hotson,	Iron Mountain, Mich.	Chapin.	Bichromate.	61.87	61.90
9	E. T. Griese,	Mountain Iron, Minn.	Mesabi.	Zimmermann-Reinhardt.	62.19	62.15
9	R. B. Green,	Minnesota Iron Co., Two Harbors, Minn.	"	"	62.12	62.15
9	C. B. Murray,	Edgar Thompson Steel Works.	"	Bichromate.	62.20	62.15
9	E. P. Jennings,	Ironwood, Mich.	"	"	62.12	62.15
9	Lerch Bros.,	Virginia, Minn.	"	Zimmermann-Reinhardt.	62.12	62.15
9	C. A. Buck,	Bethlehem Iron Co.	"	Permanganate, Jones'Reductor.	62.19	62.15
10	Average of seven chemists, Illinois Steel Co.	South Chicago, Ill.	Lake Superior Hematite.	All methods.	67.04	67.02
	" " "	" " "	Salisbury Hematite.	Bichromate.	62.65	62.70
	" " "	" " "	"	"	61.74	61.80
	" " "	" " "	"	"	61.32	61.30
	" " "	" " "	"	"	61.85	61.80
	" " "	" " "	"	"	59.27	59.30
	" " "	" " "	"	"	61.95	62.00
	" " "	" " "	"	"	62.32	62.40
	" " "	" " "	"	"	61.62	61.70
	" " "	" " "	"	"	62.22	62.30
	" " "	" " "	"	"	62.11	62.10
	" " "	" " "	"	"	62.15	62.20
	" " "	" " "	"	"	62.85	62.80
	" " "	" " "	"	"	61.44	61.50

In numbers 1 to 6, inclusive, our figures were based upon the same standard used by the respective chemist, so that the comparison between the methods is rendered independent of any difference due to the standard employed. All the rest of the analyses were based upon our own standard ore, which represents the mean of a large number of determinations, both by ourselves

and other chemists, involving a variety of modes of standardization.

The merits of the Zimmermann-Reinhardt method may be summed up as follows: (*a*) That the liquid resulting from the solution can be treated directly and without the use of special apparatus. (*b*) The operation of titration is not tedious as in the bichromate method. (*c*) That the simplicity of operation permits determinations to be made with rapidity[1] and without sacrifice of accuracy.

The authors desire to express their obligations to Dr. Harry F. Keller, of Philadelphia, Pa., for valuable suggestions made during the preparation of this paper.

LABORATORY OF MIXER AND DUBOIS,
ISHPEMING, MICH.

ON THE MANUFACTURE OF SOLUBLE NITROCELLULOSE FOR NITROGELATINE AND PLASTIC DYNAMITES.[2]

J. E. BLOMÉN, PH.D.

Received March 16, 1895.

THE discovery that a nitrocellulose could be prepared, which was soluble in a mixture of ether and alcohol, other light hydrocarbons, and in nitroglycerol, gave a start to several industries, of which not the least important was that of the manufacture of nitrogelatine, discovered by the Swede, Alfred Nobel. The use of this substance in the production of celluloid, etc., is of great importance to the industries of this country, but falls outside of the scope of this article.

In order that nitrocellulose should be easily soluble in nitroglycerol it ought to be, as nearly as possible, a pure trinitrocellulose. Higher nitration degrees are insoluble in nitroglycerol, a lower one is fully as unsatisfactory in its action and, therefore, the preparation of this substance is considered one of the most difficult problems encountered in the explosive industry. It is, in fact, considered so difficult to produce, that its manufacture is avoided by explosive companies, they preferring to buy the collodion-cotton made for celluloid manufacturing, at a high

[1] In ordinary practice in our laboratory, determinations can be made in five to ten minutes after the ore is weighed out.

[2] Read before the Washington Section, March 14, 1895.

price, in place of running the risk of a failure in manufacturing their own nitrocellulose, although if successful it could be made at a much lower cost.

As a matter of fact, the process of its manufacture is not difficult nor does it require any great chemical skill, but it does require great care in manipulation, uniformity of the materials used, and a never ceasing watchfulness of the details. The cellulose used for its preparation need not be the pure cotton used in the celluloid industry. The inferior article, known in the market as cotton-waste, is quite suitable for this purpose. To be sure the pure cotton is somewhat easier treated and requires less care in the composition of the acids used, but the difference in price between this article and the cotton-waste more than compensates for the additional handling and care. The cotton-waste must, of course, not contain too much fatty matter, but small amounts of organic acids are quite allowable as they are easily removed by suitable washing before using. To do this the bale of cotton-waste is placed in a wooden tank (cedar or best pine wood). I have found that a tank three feet high by five feet in diameter is a convenient size for this purpose. It is now washed, first, with hot water, then with a caustic soda (or sal-soda) solution, about two and one-half pounds caustic soda to a tank full of water, and again thoroughly washed with running hot water. The water having been drawn off, the cotton is taken out and dried, either by hydraulic pressure or by passing it through a centrifugal machine. It is then placed in drying rooms at a temperature of from 75° to 90° C., for at least two days, or until every particle of moisture is driven out. The next process is to pick the dried cotton into a fine fiber. For this purpose a number of cotton-picking machines are constructed and put on the market. They all possess some merits and are indispensable to a large manufacturing plant for nitrocellulose, but require capital to introduce and skilled labor to run, whereas, on the other hand, "hand-picking" is quite satisfactory, does not require initial capital, and labor otherwise wasted can easily be employed. In trying both machine-picking and hand-picking, I have found that the latter gives a more uniform result, and that (on a smaller scale at least) the time of the men waiting

for the nitration of a previous batch can be profitably used for this purpose.

As is always the case, when a number of nitro-derivatives can be obtained simply by using a stronger or weaker nitric acid and by changing the conditions under which it is used, the tri-nitro-cellulose can be obtained in several different ways. The factors to take into consideration are:

(1) The *proportion* of sulphuric and nitric acids used in the mixture.

(2) The *strength* of the two acids respectively.

(3) The *length of time* the acid mixture is allowed to be in contact with the cotton.

(4) The *temperature* maintained during the reaction.

(5) The *construction* of the plant itself; and a number of minor conditions, such as the humidity of the atmosphere at the time of the reaction.

In addition to this, there is to be taken into consideration in life, outside of the laboratory, such important items as the cheapness of plant, saving of time and economy of labor. To thoroughly investigate and finally bring each one of these conditions into such harmony that the best and most uniform product at the least expense can be produced is, in itself, a life-work and has not so far been accomplished. I will simply indicate the importance of each one of these questions and then describe *one* way, which I have found, after numberless experiments, to give satisfaction; that is, to produce a nitrocellulose soluble in nitroglycerol at a reasonable cost.

If too *much* sulphuric acid be used this is likely to attack the cotton *before* the nitric acid begins to act, converting it partly into cellulose hydrate (this will later be converted into a higher nitration degree by the nitric acid, as it is much more readily acted upon than the cellulose and will then form an insoluble nitrocellulose) and partly into glucose, which will again partly be nitrated to nitrosaccharose, which is insoluble in nitroglycerol and, besides, a very dangerous substance to have present. Again, if too *little* sulphuric acid be present it will soon form its highest hydroxide and be unable to absorb more of the water rapidly formed during the reaction, when the nitric acid will

become diluted and be unable to nitrate the cellulose. The right proportion of acid mixture is, therefore, of great importance.

If *too strong* sulphuric acid be used the result will be the same as above mentioned for an excess of it; if too strong, or too weak nitric acid be used, it is obvious that a higher or lower nitration degree than the one desired will result. It goes without saying, therefore, that the strength of the acids are of utmost importance.

In the reaction between nitric acid and cellulose no fumes are given off, except what is driven off by the heat (in which it widely differs from several other nitration processes) and although the reaction becomes feebler and, eventually, completely stops, when the acid has been diluted to a certain limit, it only gradually diminishes in force, and therefore the time has to be so balanced that the lower nitration degrees have been passed without part of the cellulose having been too highly nitrated, when it is stopped. Hence the importance of careful regulation of the time.

If the nitration pots are surrounded with water kept at a constant temperature, it will be found that the quickness and degree of the nitration depends, to a considerable extent, upon the temperature of this water. Thus, if the temperature be kept up to a high degree the nitration will be much more rapid, but at the same time experience has shown me that, in this way, a *mixture* of different nitration degrees is much more apt to result, than the uniform nitration from one degree to another. Curiously enough, the same result is obtained if no external heat at all be applied, and accordingly in my experience a carefully maintained temperature of 70° C. has been found to give the most uniform result, but no doubt good, and perhaps more economical results can be reached by elevating the temperature of the surrounding water.

It is within the experience of every chemical manufacturer, how much the size and construction of the vessels, in which the reaction takes place, influence the result, and this is fully as true in this industry as in any other. It is especially so as the cotton is so bulky that it is hard to keep every part of it in contact with the acid mixture. Under otherwise the same conditions, I have found quite a difference in the product when it was made on a

clear and dry day, and when the day was rainy or cloudy, the more so, as the building in which the operation takes place has to be left open to a great extent to allow the acid vapors to be carried away.

Even in very large dynamite works it is not always practicable to adopt the very best appliances for the manufacture of nitrocellulose, because it must necessarily be only a small part of the plant, (an average of two per cent. of the ingredients) and can only be conducted by dependence for labor, material, etc., on other parts of the works. In a large plant for the exclusive manufacture of this kind of nitrocellulose the conditions would be more favorable for improvements.

The acid mixture I have found best to use is the following: Nitric acid of 1.430 sp. gr., free from chlorine and such an amount of sulphuric acid as would influence the specific gravity, forty parts; and sixty parts of sulphuric acid of 1.835 sp. gr. The specifications for acids governing the supply for other parts of the works can be adopted for this. It is self-evident that this proportion of acids is only necessary when the work is carried on as hereinafter described and can be greatly varied under different conditions. Such an acid mixture as this cannot be stored in iron drums for any length of time and is therefore troublesome to get, if the nitric acid is not manufactured at the works. The nitric acid must be shipped in carboys; the sulphuric acid can be shipped in drums.

In mixing the two acids a sufficient quantity can be mixed at one time to last for two or three days' supply, and then stored in drums, as the acid will hardly, in this short time, affect the iron to any great extent. The mixing is best effected in a wooden tub lined with heavy lead in such a way as to allow a water-jacket of about two inches around it. (A condemned nitroglycerol apparatus with the coils removed answers this purpose very well.) If compressed air be at hand this should be used as a stirrer by placing a small perforated lead coil at the bottom of the tank and letting the air bubble through the mass since it is very difficult to get any other kind of stirrer that will stand the acids. The men should be warned to have the earthen-ware faucet at the bottom of the tank well greased, to tap it very

gently, to always use their rubber gloves and to have an ample supply of water close at hand.

This mixture although carefully made from acids of 1.430 and 1.835 sp. gr. respectively, will vary in specific gravity from 1.678 to 1.682, but if below or above this, some mistake has been made in the mixing or stirring. The nitric acid should always be dumped in the tank first and the sulphuric acid afterwards so as to give the latter a chance to mix by gravity as much as possible. Just before using, the acid mixture should be stirred again. For this purpose it is convenient to have a lead-lined tank, with an air-stirrer, of a size to hold one charge for the nitrating pots in use, in which the mixture is stirred up thoroughly and then drawn off for each pot as rapidly as possible.

The arrangement of the nitration pots, of course, must depend on existing conditions, such as size and form of the building, the size of the pots, the material used for confining the water around them, the supply of water of suitable temperature, etc. Under ordinary circumstances I have found it practicable to use earthenware pots sixteen inches deep and thirteen inches in diameter, enclosed in wooden troughs twenty feet long by twenty inches wide, connected by means of leaden pipes. If shorter it is a waste of lumber, if longer they are likely to leak from the pressure. If the troughs can conveniently be made from concrete or brickwork with water-tight mortar, of course it can be extended to any desired length.

Experience has shown two pounds to be the right amount of cotton to be used in one nitration pot. To save time and labor it is important to nitrate as much as possible at one time, but the necessity of getting a uniform product limits the amount, and as the cotton clogs or packs together as soon as wet by the acid mixture, only so much can be used at one time as will allow the mixture to act uniformly on the whole bulk of the cotton, without nitrating the outer portion too much and the inner portion too little. After having tried different amounts I have reached the conclusion that (under the given conditions) two pounds is the maximum that can safely be treated in one nitration pot.

Forty-five pounds of the well-stirred acid mixture is weighed

out and placed in the pots, which are surrounded by water heated to 70° C. The two pounds of cotton for each pot should be previously weighed out, and ready to be put in so as to have this done as nearly simultaneously as possible. It is now immersed in the acid mixture, turned about a few times with a fork and kept down by a perforated cover. The only reason for using such an excess of acids is that the cotton must be covered by it—if good covers are used forty pounds or less is enough. Besides the perforated covers, each pot should be provided with solid overlapping covers to keep back the fumes. It is now left for one hour and ten minutes, except that after thirty-five minutes the cotton is quickly turned about with the fork, a couple of times and the covers replaced. After this the nitrated cotton is quickly taken up, squeezed with the fork, and wrung out in a centrifugal machine. From this it is taken to a large-sized tank well filled with cold water, where it is thoroughly washed. It should be kept in this tank in running water for about one hour. It is well to have a large quantity of water to prevent heating by adherent sulphuric acid, but it is not so important as in the case of guncotton, because it is not so easily ignited by the heat generated nor is the acid as strong as in the latter case. It is then transferred to another tank of the same size. This is conveniently placed below and the nitrocellulose transferred on a wooden slide. Here it is washed in a sal-soda solution. From this it is taken to a pulping machine or hollender, where it is reduced to a fine pulp. This part of the process is of the greatest importance as it has been proven time and time again that if insufficiently pulped it is hard if not impossible to dissolve it in nitroglycerol. I have found that nitrocellulose, which had before been rejected as insoluble, worked very well after it had passed two or more hours in the pulp-machine. From the pulp-machine it is emptied into a large tank, allowed to settle, and the water filtered off. It is then passed either through a centrifugal machine or a hydraulic press, and thus freed from water as far as possible. It is spread in drying boxes to a depth of about two inches and kept at a temperature of about 80° C. till thoroughly dried. After that it is rubbed through fine screens until as fine as the finest flour. If treated in this way the nitrocellu-

lose will dissolve very quickly in nitroglycerol. Seven per cent. of nitrocellulose dissolves in ninety-three per cent. nitroglycerol in less than twenty minutes to a transparent jelly and three and five-tenths per cent. gives the nitroglycerol the consistency of syrup. Several hundred analyses of nitrocellulose prepared in this way show it to contain from 20.5 to 21.8 per cent. of NO_3, which very nearly corresponds to the formula of trinitrocellulose. The process carried out in this way is simple and requires no great skill or experience. The cost under ordinary circumstances and with conscientious supervision varies between thirty-five to forty cents a pound. The spent acid must of course be taken care of either by regaining it or by using it direct for other chemical processes. The only laboratory facilities that are absolutely needed are three different hydrometers, one thermometer, and a specific gravity jar—provided the acid contractors are honest.

If the nitric acid be made at the works there is no difficulty in economizing by using the lower grades made up to strength, from the acid for nitroglycerol manufacture, for instance, or from other high grades. If properly and constantly tested the waste nitroglycerol acids can be made up to strength if sufficiently strong nitric and sulphuric acids are on hand. A good and attentive chemist is certain to be able to use the products from other parts of the works (nitroglycerol works, regaining works, acid works, etc.), in such a way as to accomplish a considerable saving in the price above quoted of nitrocellulose. The conditions and facilities for making it differ, but it is safe to say that the makers can save from ten to twenty-five per cent. of the cost of manufacture in the above way by the employment of a competent chemist, to say nothing of what they save by not buying the collodion-cotton of the market at $1.00 a pound.

The best way to test the nitrocellulose for efficiency in the laboratory is undoubtedly by trying its solubility in nitroglycerol under the same conditions as prevail in the works, next to that is to note the time and result in dissolving it in an ether-alcohol mixture, and finally to use Lunge's nitrometer. The last test, though of less direct practical value, will enable the chemist to obtain a pretty good idea of what he is making and a well-

kept record of all these tests is sure to soon make it possible to always turn out a uniform product—the great desideratum in all chemical industries. The laboratory method of testing, and analysis of materials for, and products of this industry are so simple that they need not be mentioned to an assembly of chemists.

COLUMBIAN UNIVERSITY, February, 1895.

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Dr. Caldwell has made several changes in this third edition which increases the value of a book which already had much to recommend it, as the writer can testify, having used it in the laboratory for two years. Nitroso β-naphthol is added as an additional test for nickel and cobalt. It would seem as though more tests might be added for the basigens, with advantage to the student. On page 15, the equation for the oxidation of oxalic acid by potassium permanganate is not correct in this, as it was not in the former edition. The marks $\sim\!\!\cdot\!\!\sim$, $\sim\!\!-\!\!\sim$, to indicate respectively "precipitate" and "gaseous product," so far as we know entirely original with the author, are great aids to the instructor in the class-room drills. The discussions in Part I on the processes of analytical chemistry are particulary valuable, while the preliminary discussions preceding the schemes, on "the chemistry of the work" are an excellent feature. Lawrence Smith's method for alkalies is added in this edition. While the portion devoted to quantitative analysis is necessarily abbreviated in a work of this character, sufficient space is given to allow students of limited time to get a very good general knowledge of the methods employed. But we would like to have seen the determination of potash added to those of phosphorus pentoxide and nitrogen, for those interested in agricultural analysis.

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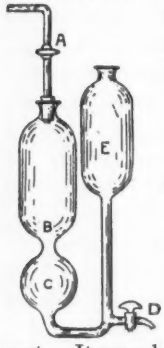
A New Hydrogen Sulphide Generator.—The accompanying figure shows a hydrogen sulphide apparatus in which objectionable features are reduced to a minimum, and the greatest convenience secured. At B is a perforated disk of lead, glass, or porcelain which supports the ferrous sulphide. When the stop-cock at A is closed, the acid is forced back by the gas into the vessel E. The globe C receives the excess of gas and prevents its bubbling back into E. When the acid is exhausted, it is drawn off at D and a new supply is added above.



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1. It is in one piece.
2. The pressure is small when the cock is closed.
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The apparatus is attached to a suitable support. It may be made of any size. The one now in use in the laboratory of Cumberland University has vessels and globe eight centimeters in diameter. It was made for me by Messrs. Eimer and Amend, New York, and is giving entire satisfaction.

CUMBERLAND UNIVERSITY,
LEBANON, TENN.

J. I. D. HINDS.

Molybdenum Carbide.—Under date of April 4th, Mr. C. H. Ehrenfeld sends the following additional information upon the supposed molybdenum carbide (see page 388 of this issue):

"Further investigation of the supposed molybdenum carbide has shown that it is undoubtedly only a mechanical mixture. Analyses of different yields of material gave no concordant results. The amount of carbon present seems to depend very largely upon the conditions under which the compound is obtained. For example, when the operation is conducted slowly, at the comparatively low temperature of a Bunsen burner, the percentage of carbon is much greater than when the material is obtained by using the high heat of a blast-lamp."

The Gas contained in Uraninite is, according to Profs. Ramsay and Crookes (*Chem. News*, **71**, 151), a mixture of helium and argon with a little nitrogen. Prof. Crookes' measurements of the helium line give, as the wave-length, 587.45, while according to Angstrom the wave-length of the helium line is 587.49, and according to Cornu 587.46. In this connection the following extract from Hillebrand's paper describing the occurrence of nitrogen in uraninite is of interest (*Am. J. Sci.*, [3], **40**, 384).

"The nitrogen is set free from the mineral as nitrogen gas by the action of a non-oxidizing inorganic acid, and by fusion with an alkaline carbonate and probably also caustic alkalies in a current of CO_2. As obtained by the use of acids the gas is colorless, odorless, a non-supporter of combustion, unchanged by mixture with air, neutral to litmus papers, not absorbed by caustic alkalies, and insoluble in water, at least its coefficient of absorption is so small as to be inappreciable without elaborate experimentation. When subjected in a eudiometer to the ordeal described by Bunsen[1] there results no alteration in volume, other than that caused by the union of the hydrogen and oxygen added.

This evidence, while fairly conclusive as to the nature of the gas, was purely negative, and proof of a more positive character was sought. Nitric acid is formed from a moist mixture of the gas with pure oxygen by long continued passage of the electric spark, and ammonia is produced by the so-called silent discharge

[1] Gasometrische Methoden, 2d ed., pp. 73 and 74.

through a mixture of the gas with three volumes of electrolytic hydrogen. The contraction produced in the latter case could be measured by cubic centimeters, and water used as an absorbent of the ammonia colored red litmus paper deep blue, besides giving a strong ammonia reaction with Nessler's reagent. With dilute hydrochloric acid as an absorbent there was obtained an abundant precipitate of ammonium platinic chloride. In a Geissler tube under a pressure of 10^{mm} and less the gas afforded the fluted spectrum of nitrogen with great brilliancy." * *

"Throughout the whole list of analyses in which nitrogen has been estimated the most striking feature is the apparent relation between it and the UO_2. This is especially marked in the table of Norwegian uraninites recalculated, from which the rule might almost be formulated that, given either nitrogen or UO_2 the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the UO_2 the higher likewise is the nitrogen."

Compounds of Argon.—Berthelot finds that argon combines with the vapor of benzene under the influence of the silent electric discharge giving a yellow resinous odorous substance condensed on the surface of the two glass tubes between which the electric action is exerted. This substance, when heated, is decomposed, leaving a bulky carbonaceous residue. The volatile products of decomposition turn litmus blue, indicating that an alkaline substance is contained in them. (From a translation of Berthelot's article in the *Chem. News*, **71**, 151.)

ERRATA.—In Professor Venable's article in the February number the name of Victor Meyer occurs in several places. It should read Lothar Meyer.

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J. I. D. HINDS.

Molybdenum Carbide.—Under date of April 4th, Mr. C. H. Ehrenfeld sends the following additional information upon the supposed molybdenum carbide (see page 388 of this issue):

"Further investigation of the supposed molybdenum carbide has shown that it is undoubtedly only a mechanical mixture. Analyses of different yields of material gave no concordant results. The amount of carbon present seems to depend very largely upon the conditions under which the compound is obtained. For example, when the operation is conducted slowly, at the comparatively low temperature of a Bunsen burner, the percentage of carbon is much greater than when the material is obtained by using the high heat of a blast-lamp."

The Gas contained in Uraninite is, according to Profs. Ramsay and Crookes (*Chem. News*, **71**, 151), a mixture of helium and argon with a little nitrogen. Prof. Crookes' measurements of the helium line give, as the wave-length, 587.45, while according to Angstrom the wave-length of the helium line is 587.49, and according to Cornu 587.46. In this connection the following extract from Hillebrand's paper describing the occurrence of nitrogen in uraninite is of interest (*Am. J. Sci.*, [3], **40**, 384).

"The nitrogen is set free from the mineral as nitrogen gas by the action of a non-oxidizing inorganic acid, and by fusion with an alkaline carbonate and probably also caustic alkalies in a current of CO_2. As obtained by the use of acids the gas is colorless, odorless, a non-supporter of combustion, unchanged by mixture with air, neutral to litmus papers, not absorbed by caustic alkalies, and insoluble in water, at least its coefficient of absorption is so small as to be inappreciable without elaborate experimentation. When subjected in a eudiometer to the ordeal described by Bunsen[1] there results no alteration in volume, other than that caused by the union of the hydrogen and oxygen added.

This evidence, while fairly conclusive as to the nature of the gas, was purely negative, and proof of a more positive character was sought. Nitric acid is formed from a moist mixture of the gas with pure oxygen by long continued passage of the electric spark, and ammonia is produced by the so-called silent discharge

[1] Gasometrische Methoden, 2d ed., pp. 73 and 74.

through a mixture of the gas with three volumes of electrolytic hydrogen. The contraction produced in the latter case could be measured by cubic centimeters, and water used as an absorbent of the ammonia colored red litmus paper deep blue, besides giving a strong ammonia reaction with Nessler's reagent. With dilute hydrochloric acid as an absorbent there was obtained an abundant precipitate of ammonium platinic chloride. In a Geissler tube under a pressure of 10^{mm} and less the gas afforded the fluted spectrum of nitrogen with great brilliancy." * *

"Throughout the whole list of analyses in which nitrogen has been estimated the most striking feature is the apparent relation between it and the UO_2. This is especially marked in the table of Norwegian uraninites recalculated, from which the rule might almost be formulated that, given either nitrogen or UO_2 the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the UO_2 the higher likewise is the nitrogen."

Compounds of Argon.—Berthelot finds that argon combines with the vapor of benzene under the influence of the silent electric discharge giving a yellow resinous odorous substance condensed on the surface of the two glass tubes between which the electric action is exerted. This substance, when heated, is decomposed, leaving a bulky carbonaceous residue. The volatile products of decomposition turn litmus blue, indicating that an alkaline substance is contained in them. (From a translation of Berthelot's article in the *Chem. News*, **71**, 151.)

ERRATA.—In Professor Venable's article in the February number the name of Victor Meyer occurs in several places. It should read Lothar Meyer.